THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR.

Volume XXI, No. 8

August, 1951

THE LIBRARY OF CONGRESS SERIAL RECORD

SEP 25 19

COPY ___

Publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

Copyright, 1952

CONSULTANTS BUREAU
152 West 42nd Street
New York 18, N. Y.

THERMAL ANALYSIS OF THE SYSTEMS

K_2MoO_4 – MoO_3, $RbMoO_4$ – MoO_3 and Cs_2MoO_4 – MoO_3

Viktor I. Spitsyn and I. M. Kuleshov

In his investigation of the Li_2MoO_4 – MoO_3 system, Hoermann found lithium di-, tri-, and tetramolybdates. These compounds are apparently unstable and exhibit no distinct maxima on the phase diagram, [1].

The Na_2MoO_4 – MoO_3 system was first investigated by Groschuff [2], who pointed out that sodium dimolybdate was formed in the system. Subsequently, Hoermann [1] confirmed Groschuff's findings, though he also assumed that tri- and tetramolybdates were present in that system. The latter exhibit blurry maxima in the phase diagram and cover a narrower range than the sodium dimolybdate.

Amadori [3] found that di-, tri-, and tetramolybdates of potassium are formed in the K_2MoO_4 – MoO_3 system. Hoermann [1], however, discovered only the trimolybdate in a subsequent investigation.

We have made a study of the phase diagrams of the Rb_2MoO_4 – MoO_3 and Cs_2MoO_4 – MoO_3 systems, which have not been described hitherto. We also investigated the K_2MoO_4 – MoO_3 system to clear up the contradictory assertions in the literature.

The thermal analysis was made by the visual-polythermal method developed by A.G.Bergman [4]. The methods of preparing the initial preparations and the results of their analyses have been set forth in our earlier papers [5,6].

1. Binary system of normal potassium molybdate and molybdic anhydride. The results of our thermal investigation of the K_2MoO_4 – MoO_3 system are set forth in Table 1 and Fig. 1. The melting points of the initial constituents are very close to those given by Hoermann for these compounds. We have found the melting point of the normal potassium molybdate to be 926°, and that of the molybdic anhydride to be 795°. As more of the molybdenum trioxide is added to the normal potassium molybdate, the liquidus curve drops rather sharply (Fig. 1) all the way down to the eutectic E_1 (467°). We discovered the following singular phenomenon on the crystallization branch of the normal salt. The crystallization of the mixture sets in long before the melt has finally solidified, in the region in which the content of molybdic anhydride is 30-45%. Some clouding is observed at about 600-500°, which disappears as cooling progresses, the molten mass turning viscous. At a still lower temperature minute heavy crystals appear at the bottom. The points at which the cloudiness first occurs in the solid phase are plotted in Fig. 1.

This phenomenon is apparently related to the polymorphic modifications of normal potassium molybdate. The γ-modification of K_2MoO_4 ought to separate out

TABLE 1

The Binary System Normal Potassium Molybdate – Molybdic Anhydride

No.	Molar % MoO_3	Crystallization temp, °C	Appearance of the separating solid phase	Remarks
1	0	926	Pointed crystals, forming cloudiness through the melt	K_2MoO_4 M.p.
2	5	901	The same	
3	10	873	The same	
4	15	840	The same	
5	20	803	The same	
6	25	759	The same	
7	30	702	The same	
8	35	639	Turbidity and formation of viscous melts	
9	38	594	The same	
10	39	577	The same	
11	40	560	The same	
12	41	545	The same	
13	42	524	The same	
14	45	467	The same	Eutectic E_1
15	46	474	Transparent rhombic lamellae on the surface of the melt	
16	47	480	The same	
17	48	486	The same	
18	49	488	The same	
19	50	489	The same	$K_2Mb_2O_7$ M.p.
20	51	487	The same	
21	52	485	The same	
22	53	481	The same	Eutectic E_2
23	54	489	Fine needles	
24	55	498	The same	
25	57.5	521	The same	
26	60	541	The same	
27	62.5	557	The same	
28	65	567	The same	
29	67.5	571	The same	$K_2MO_3O_{10}$ M.p.
30	69	567	The same	
31	70	565	The same	
32	71	560	The same	
33	72	555	The same	
34	73	553	The same	Eutectic E_3
35	74	556	Prismatic crystals	
36	75	559	The same	$K_2Mo_4O_{13}$ M.p.
37	76	556	The same	
38	77	554	The same	
39	78	547	The same	Eutectic E_4
40	79	564	The same	
41	80	579	Clusters of minute prisms	
42	81	609	The same	
43	82	625	The same	Peritectic F_1
44	83	640	Clusters of longer prisms	
45	84	649	The same	Peritectic F_2
46	85	669	Clusters of minute needles upon the surface of the melt	

(table continues on next page)

Table 1 (continued)

No.	Molar % MoO_3	Crystallization temperature, °C	Appearance of the separating solid phase	Remarks
47	87.5	697	Clusters of minute needles upon the surface of the melt	
48	90	724	The same	
49	92.5	740	The same	
50	95	764	The same	
51	100	795	The molten mass fumes considerably	Melting point of molybdic anhydride

at the temperature at which crystallization sets in in the 30-42 mol.% MoO_3 (702-524°). Its point of transition into γ-K_2MoO_4 is 480°, i.e., it lies somewhat above the eutectic (467°). It may be that γ-K_2MoO_4 forms solid solutions with potassium dimolybdate as well as viscous, readily supercooled, melts.

After the eutectic E_1 the liquidus of the K_2MoO_4 – MoO_3 system exhibits a low maximum, corresponding to potassium dimolybdate, with a melting point of 489°. This salt crystallizes out of the molten mass as transparent stub. prisms that apparently belong to the rhombic system and exist in a very narrow percentage range of the molybdic anhydride in the system (46-53 mol.%).

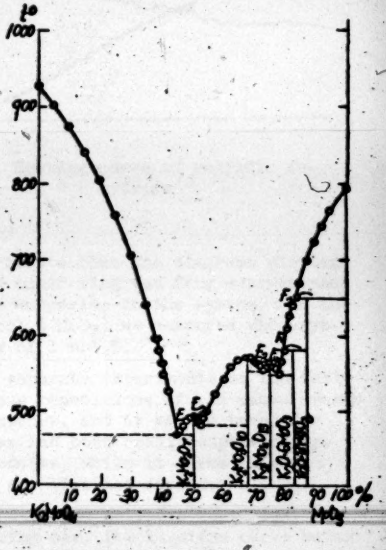


Fig. 1. Binary system: normal potassium molybdate – molybdic anhydride

The eutectic E_2 at 481° is followed by a branch of the curve that rises to a maximum representing potassium trimolybdate, with a melting point of 571°. This compound forms fine needles. The next eutectic is E_3 (553°), at 73 mol.% of molybdic anhydride in the system, after which the liquidus curve rises once more to the maximum for potassium tetramolybdate, with a melting point of 559°. Potassium tetramolybdate forms prismatic crystals that apparently belong to the monoclinic system. Its crystal clusters are sometimes arranged with their points toward the surface of the solidifying melt, resembling pointed columns. Adding more molybdic anhydride to the potassium tetramolybdate entails the lowering of the freezing point of the mixture to the eutectic E_4 (547°), after which the liquidus rises all the way up to the melting point of MoO_3, though the rise of the crystallization temperature is uneven in this portion of the diagram.

The presence of two cusps on the liquidus curve (F_1 and F_2), as well as the change in the appearance of the crystals that settle out, indicates that

unstable compounds are apparently present, most likely potassium hexa- and octamolybdates. They fuse incongruently, thus giving rise to the peritectics F_1 and F_2. Potassium hexamolybdate forms clusters of stub prisms, arranged in the shape of stars on the surface of the molten mass. The hypothetical potassium octamolybdate yields similar crystals, the prisms of which are somewhat longer.

Extrapolating the branches of the fusibility curve beyond the points F_1 and F_2, we can calculate the melting point of potassium hexamolybdate at 589°, while that of the octamolybdate is 649°. It is not impossible that the manifestation of these cusps on the final branch of the liquidus curve is due to homeomorphic [7] or polymorphic transformations of the molybdic anhydride. The heating curve of our preparation of MoO_3, however, indicates the complete absence of any transformations in the solid phase of this compound (Fig. 2).

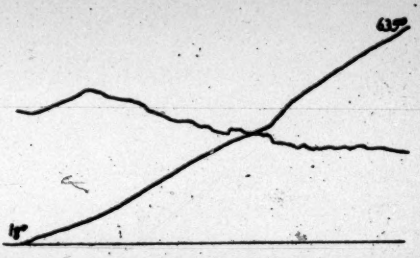


Fig. 2. Heating curve of molybdic anhydride

The phase diagram we have plotted for the K_2MoO_4 – MoO_3 system is more accurate than the diagrams plotted by Hoermann and Amadori. These authors plotted their diagrams from experimental data taken at intervals of 10 mol.% of molybdic anhydride in the system. In the most important sections of the diagram (40-90 mol.% MoO_3) we measured the crystallization points of the mixtures at intervals of 1 mol.%.

Identical results were obtained in three separate experiments on the fusibility of the K_2MoO_4 – MoO_3 system, plus numerous repetitions of the measurements of individual crystallization points of the mixtures, and it may be taken for granted that the system is more complicated than had been realized previously. It contains potassium di-, tri-, and tetramolybdates, while it seems that the less stable potassium hexa- and octamolybdates are likewise formed.

2. Binary system of normal rubidium molybdate and molybdic anhydride. In many ways this system reminds one of the preceding one, its liquidus curve being almost the same. The slight difference boils down to a less prominent maximum for rubidium molybdate and a slight lowering of the temperature of crystallization for the other isopolymolybdates. Table 2 and Fig. 3 give the results of our thermal investigation of the Rb_2MoO_4 – MoO_3 system.

The melting point of normal rubidium molybdate was found to be 929°. In this system, as in the previous one, we found four eutectic arrest points and two peritectics, F_1 and F_2. The first eutectic point E_1 (458°) is located at 44 mol.% of molybdic anhydride, the second E_2 (478°) at 51 mol.% of MoO_3, the third E_3 (549°) at 73 mol.%, and the fourth E_4 (546°) at 79 mol.%.

When we compare the liquidus curve for the system of normal rubidium molybdate and molybdic anhydride with the similar curve for the preceding potassium system, we note that nearly all the characteristic points of the two systems repeat in the same order. The rubidium system likewise displays the di-, tri-, and tetramolybdates, the hexa- and octamolybdates also being present, apparently.

Rubidium dimolybdate forms lustrous colorless rhombic lamellae on the

TABLE 2

The Binary System Normal Rubidium Molybdate – Molybdic Anhydride

No.	Molar % MoO_3	Crystallization temp, °C	Appearance of the separating solid phase	Remarks
1	0	929	Minute pointed crystals	Rb_2MoO_4 M.p.
2	5	909	The same	
3	10	873	The same	
4	15	837	The same	
5	20	796	The same	—
6	25	754	The same	
7	30	705	The same	
8	35	644	Turbidity, with ensuing viscous melts	
9	37.5	611	The same	
10	39	587	The same	
11	40	570	The same	
12	41	546	The same	
13	42	524	The same	
14	43	500	The same	
15	44	458	The same	Eutectic E_1
16	45	460	Lustrous rhombic lamellae form on the surface of the melt. Stub prisms throughout the melt	
17	46	465	The same	
18	47	470	The same	
19	48	473	The same	
20	49	477	The same	
21	50	479	The same	$Rb_2Mo_2O_7$ M.p.
22	51	478	The same	Eutectic E_2
23	52	487	Fine acicular crystals throughout the melt	
24	53	496	The same	
25	54	506	The same	
26	55	517	The same	
27	57.5	532	The same	
28	60	545	The same	
29	62.5	556	The same	
30	65	560	The same	
31	67.5	563	The same	$Rb_2Mo_3O_{10}$ M.p.
32	69	562	The same	
33	70	558	The same	
34	71	555	The same	
35	72	552	The same	
36	73	549	The same	Eutectic E_3
37	74	552	Yellow prismatic crystals	
38	75	554	The same	$Rb_2Mo_4O_{13}$ M.p.
39	76	553	The same	
40	77	550	The same	
41	78	546	The same	Eutectic E_4
42	79	554	Clusters of minute prisms	
43	80	562	The same	
44	81	569	The same	
45	82	583	The same	Peritectic P_1
46	83	593	Clusters of longer prisms	
47	84	604	The same	

(table continues on next page)

Table 2 (continued)

No.	Molar % MoO_3	Crystallization temp., °C	Appearance of the separating solid phase	Remarks
48	85	610	Clusters of longer prisms	
49	86	624	Clusters of minute needles	Peritectic F_2
50	87.5	655	The same	
51	90	692	The same	
52	92.5	722	The same	
53	95	750	The same	
54	100	795	The molten mass fumes considerably	MoO_3 M.p.

surface of the melt. The trimolybdate crystallizes as thin acicular crystals. The prismatic crystals of the tetramolybdate are gray. The hexa- and octamolybdates form clusters of prisms, the prisms being longer in the octamolybdate.

The melting points of rubidium di-, tri-, and tetramolybdates: 479, 563, and 554°, respectively, average some 5-10° higher than the melting points of the analogous isopolymolybdates of potassium. The difference between the melting points of the unstable hexa- and octamolybdates of rubidium and potassium is greater, the corresponding rubidium compounds fusing at some 20-40° less (575 and 617°). Viscous melts, like those noted in the K_2MoO_4 – MoO_3 system, are observed close to the eutectic E_1 along the branch of the curve at which the normal rubidium molybdate crystallized.

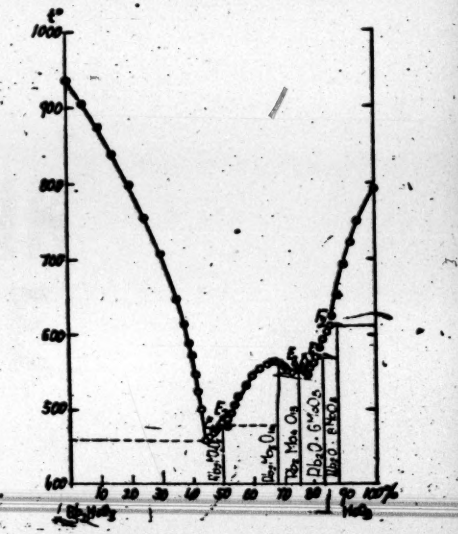


Fig. 3. The binary system normal rubidium molybdate – molybdic anhydride

3. The binary system of normal cesium molybdate and molybdic anhydride. This system differs from the preceding ones in not possessing a maximum corresponding to a cesium dimolybdate. Nor are the maxima for the other isopolymolybdates very distinct, as was the case in the analogous system for the potassium molybdates. They all lie at lower temperatures. The results of our thermal analysis of the Cs_2MoO_4 – MoO_3 system are set forth in Table 3 and Fig. 4.

We found the melting point of normal cesium molybdate to be 925°.

Three eutectic points were found in this system. The first eutectic E_1 (458°) was located at 45 mol.% of MoO_3, the second E_2 (523°) at 72 mol.%, and the third E_3 (530°) at 77 mol.%. The liquidus curve of the Cs_2MoO_4 – MoO_3 system also exhibited two peritectic points, F_1 and F_2, at 82 and 84 mol.% of MoO_3. They demarcate regions of unstable compounds: cesium hexa- and octamolybdates, as we assumed.

TABLE 3

Binary System Normal Cesium Molybdate – Molybdic Anhydride

No.	Molar % MoO_3	Crystallization temp., °C	Appearance of the separating solid phase	Remarks
1	0	925	Scattered pointed crystals	Cs_2MoO_4 m.p.
2	5	902	The same	
3	10	866	The same	
4	15	827	The same	
5	20	785	The same	
6	25	734	The same	
7	30	679	The same	
8	35	624	The same	
9	39	567	Turbidity sets in long before final crystallization, followed by formation of viscous melts. Prominent needles in solidified mass.	
10	40	553	The same	
11	41	529	The same	
12	42	506	The same	
13	43	491	The same	
14	44	470	The same	
15	45	458	The same	Eutectic E_1
16	46	472	Acicular crystals	
17	47	479	The same	
18	48	484	The same	
19	49	488	The same	
20	50	494	The same	
21	51	499	The same	
22	52	505	The same	
23	53	509	The same	
24	55	517	The same	
25	57.5	527	The same	
26	60	537	The same	
27	62.5	542	The same	
28	65	544	The same	
29	67.5	545	The same	$Cs_2Mo_3O_{10}$ M.p.
30	69	543	The same	
31	70	539	The same	
32	71	535	The same	
33	72	523	The same	Eutectic E_2
34	73	529	Prismatic crystals	
35	74	532	The same	
36	75	534	The same	$Cs_2Mo_4O_{13}$ M.p.
37	76	532	The same	
38	77	530	The same	Eutectic E_3
39	78	539	Clusters of stub prisms	
40	79	546	The same	
41	80	550	The same	Peritectic P_1
42	81	560	The same	
43	82	567	The same	
44	83	571	Clusters of longer prisms	
45	84	575	The same	Peritectic P_2
46	85	593	The same	
47	87.5	630	Clusters of minute needles	
48	90	678	The same	
49	92.5	708	The same	
50	95	742	The same	
51	100	795	The melt fumes considerably	MoO_3 M.p.

The maximum representing the cesium tri- and tetramolybdates on the liquidus curve of this system are located at 545 and 534°, respectively, or 18-20° lower than the melting points of the analogous isopolymolybdates of rubidium. The melting points of the hypothetical hexa- and octamolybdates of cesium are taken to be 556 and 581°, respectively.

Cesium trimolybdate forms fine acicular crystals, while the theramolybdate crystallized in prisms. Cesium hexamolybdate consists of clusters of stub prisms, while the octamolybdate consists of clusters of longer prisms.

The pyrometric investigation of some of the alloys with the N.S.Kurnakov automatic recording pyrometer confirmed the results secured by the visual polythermal method. The heating curves of mixtures of cesium molybdate and molybdic anhydride, the compositions of which lay in the regions of viscous melts (37-45 mol.% MoO_3), displayed the sloping areas that are characteristic of solid solutions. This bears out the supposition expressed above regarding the reasons for the formation of viscous melts on the crystallization curve for the normal molybdate near the eutectic point.

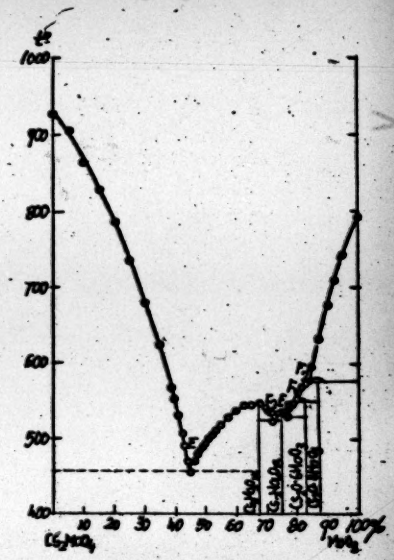


Fig. 4. The binary system normal cesium molybdate – molybdic anhydride.

The behavior of the cesium isopolymolybdates below the liquidus was also of interest. In the region representing the existence of the tri- and tetramolybdates, an exothermal effect (Fig. 5) is observed along the heating curve of the respective melts, no matter what their composition was.

This phenomenon is apparently due to the fact that the acid molybdates of cesium crystallized from the melt undergo partial or complete decomposition as cooling continues into the normal cesium molybdate and molybdic anhydride or into a more stable acid molybdate. When the resultant mixture of compounds is heated, an exothermic reaction involving the formation of cesium acid molybdates evidently occurs at 370°. It may be that this phenomenon occurs in all systems that contain acid molybdates.

Table 4 gives the melting points of the compounds we have investigated.

TABLE 4

Melting Points of Potassium, Rubidium, and Cesium Molybdates

Cation	Melting points of various types of molybdates					
	Me_2MoO_4	$Me_2Mo_2O_7$	$Me_2Mo_3O_{10}$	$Me_2Mo_4O_{13}$	$Me_2Mo_6O_{19}$	$Me_2Mo_8O_{25}$
K	926°	489°	571°	559°	589° •	649° •
Rb	929	479	563	554	575 •	617 •
Cs	925	–	545	534	556 •	581 •

• Melting point extrapolated from the cusps on the liquidus curve.

It will be noticed that the melting points of the acid molybdates of potassium, rubidium, and cesium are far below those for the normal molybdates. The melting points of the isopolymolybdates rise as their percentages of molybdic anhydride rises, the sole exception being the tetramolybdates, whose melting points are lower than those of the trimolybdates.

To judge by the nature of the phase diagrams cited, most of the acid molybdates discovered by the method of thermal analysis melt with decomposition. This is especially true of the hexa- and octamolybdates, which have been detected at the cusps on the liquidus curves. The most stable are most likely the trimolybdates of of potassium, rubidium, and cesium.

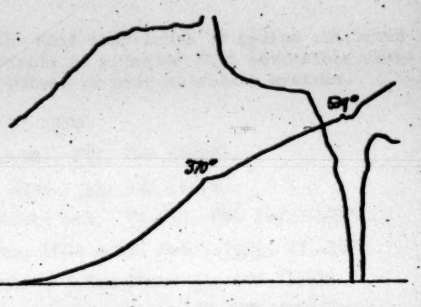


Fig. 5. Heating curve of an alloy of acid molybdates (72 mol.% MoO_3).

The normal molybdates of potassium, rubidium, and cesium fuse within an extremely narrow range (925-929°). The melting point drops in all the isopolymolybdates as we pass from the potassium compounds to the rubidium and cesium compounds. This phenomenon is apparently due to the decrease in the stability of the space lattices as the ionic radii of the alkali elements are increased.

Comparing the results of the present investigation with the data in the literature on the composition of the acid molybdates of lithium and sodium, we may state that the alkali elements form the following isopolymolybdates, crystallized from their melts:

$Li_2Mo_2O_7$	$Na_2Mo_2O_7$	$K_2Mo_2O_7$	$Rb_2Mo_2O_7$	—
$Li_2Mo_3O_{10}$	$Na_2Mo_3O_{10}$	$K_2Mo_3O_{10}$	$Rb_2Mo_3O_{10}$	$Cs_2Mo_3O_{10}$
$Li_2Mo_4O_{13}$	$Na_2Mo_4O_{13}$	$K_2Mo_4O_{13}$	$Rb_2Mo_4O_{13}$	$Cs_2Mo_4O_{13}$
—	—	$K_2Mo_6O_{19}$	$Rb_2Mo_6O_{19}$	$Cs_2Mo_6O_{19}$
—	—	$K_2Mo_8O_{25}$	$Rb_2Mo_8O_{25}$	$Cs_2Mo_8O_{25}$

As the ionic radii of the alkali elements grow larger, there is an increasing tendency for them to form more highly acid molybdates, while the dimolybdates become less stable apparently.

SUMMARY

1. The K_2MoO_4 – MoO_3, Rb_2MoO_4 – MoO_3, and Cs_2MoO_4 – MoO_3 systems have been investigated by the method of thermal analysis.

2. In contrast to the latest data in the literature, the system K_2MoO_4 – MoO_3 has been found to contain the di-, tri-, and tetramolybdates of potassium, as well as the unstable hexa- and octamolybdates.

3. The liquidus curve of the Rb_2Mo_4 – MoO_3 system resembles the corresponding curve for the K_2MoO_4 – MoO_3 system.

4. Cesium does not form a dimolybdate. Otherwise, the Cs_2MoO_4 – MoO_3

system exhibits the same compounds as the rubidium one.

5. The crystalline forms of the molybdates of potassium, rubidium, and cesium have been described, and some regularities in the behavior patterns of their melting points have been set forth.

6. The heating curves of melts of the acid molybdates of cesium exhibited an exothermal effect at 370°. The hypothesis is advanced that reversible chemical transformations occur in the solid phases in acid molybdate systems.

LITERATURE CITED

[1] F.Hoermann, Z. allgem. anorg. Chem., 177, 145 (1929).

[2] E.Groschuff, Z. allgem. anorg. Chem., 58, 113 (1908).

[3] M. Amadori, Atti. reale ist. Veneto sci. 72, II, 896 (1912-1913).

[4] A.G.Bergman, Trans. June Session, USSR Acad. Sci., 1932, II, 167.

[5] Viktor I. Spitsyn and I.M.Kuleshov, J.Gen.Chem. 21, 408 (1951).*

[6] Viktor I.Spitsyn and I.M.Kuleshov, J.Gen.Chem. 21, 401 (1951).**

[7] A.G.Bergman, Proc. USSR Acad. Sci., 35, 307 (1942).

Received October 2, 1949.

Laboratory of Inorganic Chemistry
The M.V.Lomonosov State University
of Moscow
Awarded the Order of Lenin

* See C.B. Translation, p. 453
** See C.B. Translation, p. 445.

THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$, and $AsCl_3$

VI. THE $AsCl_3$ - CCl_3COOH SYSTEM

T. Sumarokova and A. Babkov

The present paper gives the results of a study of the viscosity and density in the $AsCl_3$ - CCl_3COOH system at 20, 35, and 60°, by way of comparison with the $SbCl_3$ - CCl_3COOH system [1].

The arsenic trichloride was twice distilled and sealed in an ampoule.

The results of the viscosity measurements are listed in Table 1.

TABLE 1

Viscosity of the $AsCl_3$ - CCl_3COOH System

Mol. % $AsCl_3$	$\eta \cdot 10^2$		
	20°	35°	60°
100.00	12.26	10.50	8.05
86.07	14.03	11.53	8.51
74.74	16.21	13.61	9.52
68.85	18.71	14.79	9.93
63.80	19.52	15.56	10.51
56.25	22.92	18.01	12.19
39.24	35.44	25.92	15.95
22.11	Crystals	40.39	22.76
8.26	Crystals	Crystals	32.48
0.00	Crystals	Crystals	38.65

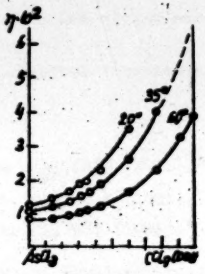


Fig. 1.

The variation of viscosity with composition is represented in Fig. 1. As we see from the figure, the viscosity drops uniformly from CCl_3COOH to $AsCl_3$. The viscosity isotherms are convex to the axis of composition for all temperatures.

The absence of conductivity in the system indicates that the system constituents do not react with each other, as the latter results in the setting up of conductivity in the analogous systems formed by $SbCl_3$ and CH_3COOH, $CH_2ClCOOH$, and CCl_3COOH [1,2,3].

The density data are tabulated in Table 2.

The variation of the specific volume with the composition (in wt. %) is represented by the straight line in Fig. 2.

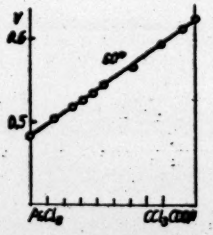


Fig. 2.

TABLE 2

Density of Mixtures of $AsCl_3$ and CCl_3COOH

Mol. % $AsCl_3$	d		
	20°	35°	60°
100.00	2.1624	2.1231	2.0624
86.07	2,0749	2.0431	1.9957
74.74	2.0106	1.9820	1.9419
68.85	1.9896	1.9623	1.9050
63.80	1.9621	1.9251	1.8851
56.25	1.9159	1.8842	1.8462
39.24	1.8279	1.8043	1.7709
22.11	Crystals	1.7258	1.6872
8.26	Crystals	Crystals	1.6344
0.00	Crystals	Crystals	1.6051

An investigation of the viscosity and density of the $AsCl_3$ – CCl_3COOH system has, therefore, indicated that the system constituents do not interact with each other.

SUMMARY

1. The viscosity and density of the $AsCl_3$ – CCl_3COOH system has been investigated at 20, 35, and 60°.

2. The resulting diagrams establish that no chemical interaction between the constituents occurs in this system.

LITERATURE CITED

[1] M.Usanovich and T.Sumarokova, J.Gen.Chem. 21, 1219 (1951).*

[2] M.Usanovich and T.Sumarokova, J.Gen.Chem. 21, 1214 (1951).*

[3] T.Sumarokova and M.Usanovich, J.Gen.Chem. 21, 987 (1951).*

Received August 6, 1949.

Laboratory of Physical Chemistry
Central Asian State University.

* See C.B.Translation.

THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$, and $AsCl_3$

VII. THE $AsCl_3$ – $CH_2ClCOOH$ and $AsCl_3$ – CH_3COOH SYSTEMS

T. Sumarokova and the Student V. Glushchenko

Monochloroacetic acid was purified by triple distillation, the fraction with a boiling point of 182° at 688 mm pressure being collected and sealed into ampoules. The constants of the monochloroacetic acid were as follows: d_{50}^{4} 1.3907, η_{50}^{4} 0.03091. The acetic acid was desiccated with calcined $CuSO_4$, distilled, and then subjected to fractional freezing, and sealed into ampoules. The constants of the acid were as follows: m.p. 16.35°, d_{20}^{4} 1.0489, η_{20}^{4} 0.01209. The arsenic trichloride was purified by triple distillation, the fraction with a b.p. of 125° at 676 mm being collected and sealed into ampoules. The constants of the arsenic trichloride were as follows: d_{20}^{4} 2.1647 and η_{20}^{4} 0.0103.

a) The $AsCl_3$ – $CH_2ClCOOH$ system proved to be a nonconductor; its viscosity and density were investigated at 50, 60°, and 70°. The results of our measurements of the viscosity of the $AsCl_3$ – $CH_2ClCOOH$ system are listed in Table 1 and represented graphically in Fig. 1. The density data are listed in Table 2.

TABLE 1

Mol. % $AsCl_3$	$\eta \cdot 10^2$		
	50°	60°	70°
100.00	0.822	0.745	0.689
78.40	1.003	0.894	0.812
70.27	1.084	0.965	0.867
66.66	1.140	1.013	0.907
54.00	1.340	1.166	1.016
45.43	1.387	1.198	1.056
35.53	1.756	1.485	1.281
21.54	–	1.774	1.521
20.70	2.191	1.809	1.541
14.34	–	1.989	1.678
10.82	2.650	2.135	1.779
8.40	–	2.222	1.844
5.70	–	2.292	1.902
4.32	–	2.328	1.955
0.00	3.091	2.446.	2.051

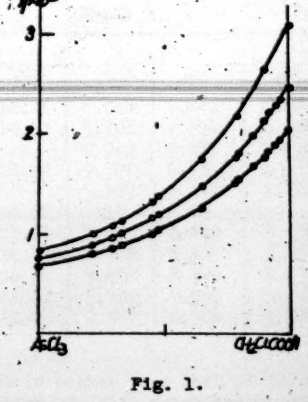


Fig. 1.

The viscosity of this system rises uniformly from $AsCl_3$ to $CH_2ClCOOH$, the isotherms being curves convex toward the composition axis.

As the temperature is raised, the viscosity diminishes greatly in the region of the monochloroacetic acid. The absence of conductivity and the sagging shape of the viscosity isotherm indicate that there is no chemical interaction in the system. The linear nature of the variation of the specific volume with composition (Fig. 2) is evidence that no molecular changes occur in the system.

TABLE 2

Mol. % $AsCl_3$	Wt.% $AsCl_3$	d		
		50°	60°	70°
100.00	100.00	2.0995	2.0785	2.0583
78.40	87.10	1.9708	1.9515	1.9317
70.27	81.93	1.9500	1.9004	1.8809
66.66	79.33	1.9011	1.8797	1.8587
54.00	69.26	1.8156	1.7975	1.7791
45.43	67.89	1.8076	1.7900	1.7720
34.53	50.32	1.6735	1.6579	1.6411
21.54	34.51	1.5752	1.5607	1.5461
14.34	24.31	1.5124	1.5030	1.4860
10.82	18.60	-	1.4690	1.4564
8.40	15.00	-	1.4465	1.4333
5.70	10.68	-	1.4229	-
4.32	1.97	-	1.4115	1.3991

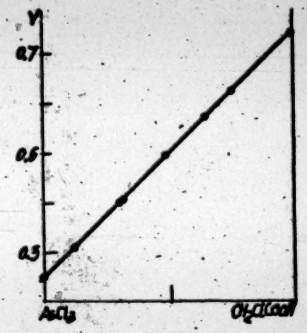


Fig. 2

b) The $AsCl_3$ – CH_3COOH system's conductivity, viscosity, and density were investigated at 20, 50, 60, and 70°. The results of the viscosity measurements are given in Table 3. Fig. 3 shows the variations of viscosity with composition. We see in the Figure that the viscosity isotherms pass through a maximum (at 40-50 mol.% $AsCl_3$), which shifts toward the more viscous constituent $AsCl_3$ as the temperature is raised. Inasmuch as the temperature coefficient of viscosity

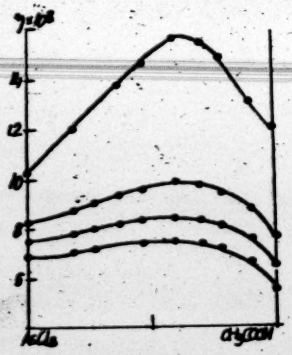


Fig. 3.

TABLE 3

Mol.% $AsCl_3$	$\eta \cdot 10^3$			
	20°	50°	60°	70°
100.00	10.25	8.218	7.449	6.887
81.25	12.13	8.728	7.796	7.024
72.90	-	9.005	7.933	7.197
63.10	13.78	9.325	8.191	-
53.63	-	9.237	8.319	7.367
52.90	14.66	-	-	-
40.70	15.62	9.820	8.409	7.432
29.90	15.41	9.702	8.304	7.277
21.74	14.87	9.460	8.120	7.131
9.83	13.12	8.793	7.599	6.679
0.00	12.09	7.650	6.500	5.500

of CH_3COOH is higher than that of $AsCl_3$, the viscosity of $AsCl_3$ exceeds that of CH_3COOH at 50 and 60°. The presence of a viscosity maximum indicates that interaction takes place within the system.

The fact that the $AsCl_3$ – CH_3COOH system is a conductor shows that the interaction is of an acid-basic nature.

The conductivity of the $AsCl_3$ – CH_3COOH system was investigated at 50 and 60°. The mixtures were prepared by successively adding CH_3COOH to a given amount of $AsCl_3$ directly in the vessel used for the conductance measurements. The conductance measurement data are listed in Table 4. Table 4 and Fig. 4, which plots the conductance as a function of the composition, indicate that the conductance isotherms are complex. They traverse a maximum located at approximately 60 mol.% $AsCl_3$ and a point of inflection at 50 mol.% $AsCl_3$. The specific conductance drops as the temperature rises, the conductance maximum shifting toward the $AsCl_3$ side of the graph. The conductance isotherms grow simpler when a viscosity correction is applied. The isotherms of the corrected conductance (Fig. 5) traverse a maximum located at approximately 58-60 mol. % $AsCl_3$.

The data on the corrected conductance are listed in Table 5. We do not reproduce the figures for the temperature coefficient, as its value is low (about 1%) and varies but little with concentration.

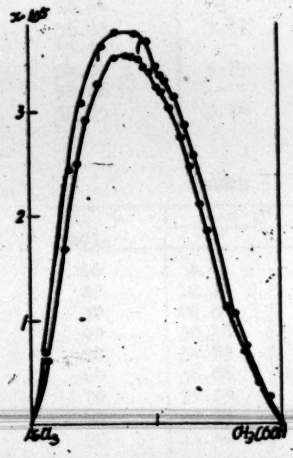


Fig. 4.

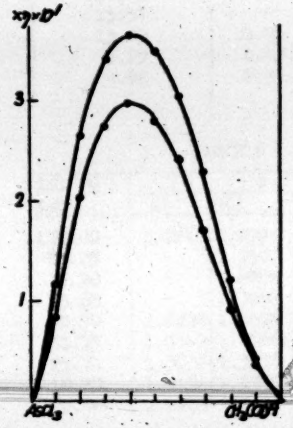


Fig. 5.

The results of our density measurements are given in Table 6. Figure 6 plots the specific volume as a function of the composition, expressed in per cent by weight. We see in the figure that shrinkage occurs in the system, due to interaction of the system constituents.

Hence, the data on the conductivity, viscosity, and density lead us to conclude that the system components enter into acid-basic interaction with each other, the $AsCl_3$ acting as an acid. We secured no data on the composition of any compounds.

Comparison of the results obtained in our studies of the $AsCl_3$ – $CH_2ClCOOH$, $AsCl_3$ – CH_3COOH, and $AsCl_3$ – CCl_3COOH indicates that of the three acids (CH_3COOH, $CH_2ClCOOH$, and CCl_3COOH) only CH_3COOH manifests basic properties with respect to $AsCl_3$.

TABLE 4

Mol. % $AsCl_3$	$\kappa \cdot 10^5$		Mol. % $AsCl_3$	$\kappa \cdot 10^5$	
	50°	60°		50°	60°
100.00	–	–	49.97	3.59	–
93.13	0.69	0.64	49.39	–	3.35
86.53	–	1.73	47.60	3.41	–
83.25	2.53	–	47.34	–	3.28
80.72	–	2.56	45.03	3.36	–
77.09	3.18	–	44.12	–	3.11
75.70	–	2.98	41.82	3.22	–
71.17	–	3.44	39.81	–	2.82
70.45	3.73	–	38.51	2.94	–
66.80	4.03	–	35.41	–	2.54
65.25	–	3.63	34.38	2.65	–
63.96	3.85	–	28.41	–	1.94
60.97	–	3.63	28.22	1.85	–
59.02	3.95	–	21.32	–	1.31
58.64	–	3.58	19.89	1.13	–
56.63	3.87	–	18.09	1.06	–
55.92	–	3.54	13.57	–	0.71
54.84	3.79	–	13.29	0.76	–
52.66	–	3.44	8.29	0.40	0.42
52.65	3.78	–	4.42	0.33	0.38

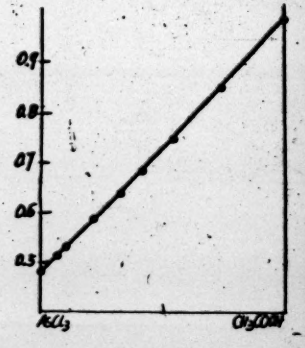
TABLE 5*

Mol. % $AsCl_3$	$\kappa\eta \cdot 10^7$	
	50°	60°
10	4.44	3.80
20	12.69	9.32
30	22.85	17.02
40	30.46	23.94
50	34.83	27.88
60	36.66	29.52
70	34.03	27.20
80	26.25	20.28
90	11.40	8.36

* The corrected conductance values were secured graphically.

TABLE 6

Mol. % $AsCl_3$	d			
	20°	50°	60°	70°
100.00	2.1646	2.0995	2.0785	2.0583
81.25	–	1.9593	1.9387	1.9177
72.90	–	1.8864	1.8666	1.8468
53.63	–	1.7068	1.6880	1.6680
40.70	1.6230	1.5696	1.5509	1.5332
31.77	1.5142	1.4666	1.4454	1.4297
21.74	1.3835	1.3376	1.3240	1.3070
10.30	1.2165	1.1752	1.1628	1.1514
0.00	1.0489	1.0154	1.0058	0.9925



SUMMARY

1. A study has been made of the viscosity and density of the $AsCl_3$ – $CH_2ClCOOH$ system at 50, 60, and 70°. The absence of conductivity and the shape of the viscosity and density isotherms indicate that the system components do not interact with each other.

2. A study has been made of the conductance of the $AsCl_3$ – CH_3COOH system at 50 and 60°, and of its density and viscosity at 20, 50, 60, and 70°. Acid-basic interaction has been found to exist in this system.

LITERATURE CITED

[1] T.Sumarokova and A.Babkov, J.Gen. Chem. 21, 1375 (1951).

Received August 6, 1949.

Laboratory of Physical Chemistry, Institute of Chemistry, Kazakh Academy of Sciences

THE REACTIONS OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM IN THE MOLTEN STATE

II. Investigation of the Ternary System Consisting of the Nitrates of Strontium - Potassium - Sodium in the Molten State

P. I. Protsenko and A. G. Bergman

Not much research has been done on the chemistry of nitrates and nitrites in the molten state. According to the references in the handbook literature available to us [1,2,3,4,5,6], a total of 35 binary and 6 ternary systems has been investigated. The investigations carried out by various authors on nitrate-nitrite salt equilibria are of an incidental character, without the general idea of explaining the nature of chemical interaction between nitrate - nitrite constituents of melts as a function of the position of the respective elements in the Mendeleev periodic system. Only in the papers by A.P.Palkin [6,7] on binary systems consisting of silver nitrates, on the one hand, and nitrates of the alkali metals, on the other, do we find an indication of a pattern of behavior in the change of the nature of chemical interaction as the atomic weight of the alkali metal increases. Filling this gap in our knowledge of the chemistry of molten salts became a natural objective.

The present paper is a continuation of systematic researches in the equilibrium state in systems consisting of nitrates and nitrites of metals in the first and second groups of the D.I.Mendeleev periodic system, carried out by one of the present authors. The study of the behavior of nitrates of strontium, potassium, and sodium in the molten state had as its objective the ascertaining of the nature of the chemical interaction occurring between the nitrates of the foregoing metals in binary and ternary combinations, as well as adding further factual material on ternary salt equilibria, required to disclose the general behavior patterns existing in the chemistry of nitrates and nitrites in the molten state.

Harkins and Clark [3] made a study of the fusibility diagram of the ternary system consisting of the nitrates of strontium, potassium, and sodium [3]. This investigation was never completed, however.

Incomplete and insufficiently precise measurements of the binary systems: strontium nitrate - potassium nitrate, and strontium nitrate - sodium nitrate, have been made by N.A.Dailidovich and M.A.Nikitin [8]. We therefore set as our objective a careful investigation of the whole ternary fusibility diagram.

Binary systems. The strontium nitrate - sodium nitrate binary system has two branches of the crystallization curve - a short branch for the crystallization of sodium nitrate, dropping uniformly to the eutectic point at 287° and a composition of 90.5 mol.% of sodium nitrate and 9.5 mol.% of strontium nitrate, and

long crystallization branch for the strontium nitrate, rising sharply to the ordinate for the composition of 50 mol.% of strontium nitrate.* This latter composition is reached at 480°. When the molten salts of strontium and sodium nitrate were heated above 480°, any further addition of strontium nitrate resulted in decomposition of the salts, indicated by the dotted lines on the liquidus curve (Fig. 1 and Table 1). The melts of strontium and sodium nitrate are colorless, transparent, and readily crystallizable.

TABLE 1

(Eutectic: 287°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	Equimolecular per cent $(NaNO_3)_2$	Temp. at which first crystals settled out	Point No.	Equimolecular per cent $Sr(NO_3)_2$	Equimolecular per cent $(NaNO_3)_2$	Temp. at which first crystals settled out
1	0	100	308°	13	14	86	321°
2	3	97	305	14	16	84	331
3	5	95	302	15	18	82	342
4	6	94	300	16	20	80	352
5	7	93	297	17	22	78	365
6	8	92	295	18	25	75	377
7	9	91	292	19	30	70	396
8	9.5	90.5	287	20	35	65	420
9	10	90	291	21	40	60	442
10	11	89	298	22	45	55	460
11	12	88	305	23	50	50	480
12	13	87	312				

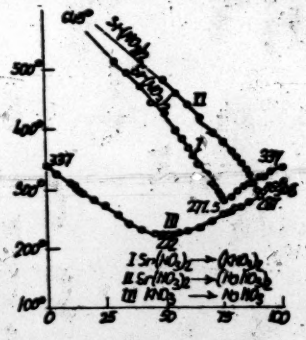


Fig. 1.

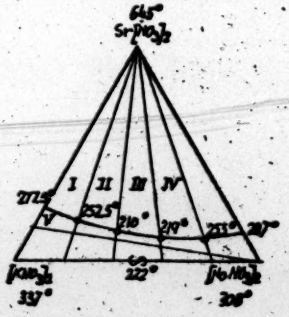


Fig. 2.

The strontium nitrate – potassium nitrate binary system has two crystallization branches – a short branch representing the crystallization of potassium nitrate, which is flat at first, but then drops sharply to the eutectic point at 277.5° and a composition of 25% strontium nitrate and 75% potassium nitrate, and a long branch for the crystallization of strontium nitrate, which rises steeply to the ordinate for the composition of 70% strontium nitrate. At a point directly below this composition perceptible decomposition of the metal nets in at 513°,

---

* Henceforth all compositions are given in equimolecular percentages.

with the evolution of oxygen. In the fusibility diagram of the system, the liquidus curve is shown by a dotted line beyond the point where decomposition sets in (Fig. 1 and Table 2).

TABLE 2

(Eutectic: 277.5°)

Point No.	Equimolecular per cent		Temp. at which first crystals settle out	Point No.	Equimolecular per cent		Temp. at which first crystals settle out
	$Sr(NO_3)_2$	$(KNO_3)_2$			$Sr(NO_3)_2$	$(KNO_3)_2$	
1	0	100	337°	14	29	71	304°
2	5	95	326	15	30	70	308
3	7.5	92.5	320	16	32.5	67.5	324
4	10	90	316	17	35	65	338
5	12.5	87.5	311	18	37.5	62.5	354
6	15	85	306	19	40	60	369
7	17.5	82.5	301	20	42.5	57.5	384
8	20	80	295	21	45	55	400
9	22.5	77.5	291	22	50	50	424
10	25	75	278	23	55	45	447
11	26	74	284	24	60	40	472
12	27	73	290	25	65	35	494
13	28	72	294	26	70	30	513

The melts of strontium and potassium nitrates are also transparent and colorless and crystallize readily all along both liquidus curves.

The sodium nitrate – sodium nitrite system has been described by the present authors previously [8] (Fig. 1).

We investigated five ternary sections to determine the nature of the interaction of the nitrates of strontium, potassium, and sodium in a ternary molten mass and to study the liquidus surface. Sections I, II, III, and IV from the $Sr(NO_3)_2$ vertex to the potassium nitrate – sodium nitrate side of the triangle were investigated, as was section V from the potassium nitrate – strontium nitrate side of the triangle to the $(NaNO_3)_2$ vertex (Fig. 2).

Sections I, II, III, and IV were drawn in order to find the line demarcating the crystallization areas of the strontium, potassium, and sodium nitrates.

Ternary sections. Section I: 20% $(NaNO_3)_2$ + 80% $(KNO_3)_2$ → $Sr(NO_3)_2$, exhibits two crystallization branches: a short one for the crystallization of solid solutions of potassium and sodium nitrates, which drops rectilinearly to the transition point, and the crystallization branch of strontium nitrate, which rises steeply to the composition ordinate for 65% strontium nitrate. The transition point is located at 252.5° and a composition of 16.5% sodium nitrate, 66% potassium nitrate, and 17.5% strontium nitrate.

The melting points of the molten salts along the section line I have been investigated up to 497°. The salts decompose above that temperature (Table 3, Fig. 3).

Section II: 40% $(NaNO_3)_2$ + 60% $(KNO_3)_2$ → $Sr(NO_3)_2$, has two crystallization branches: a branch for the crystallization of solid solutions of potassium and sodium nitrates, and another for strontium nitrate, which is somewhat convex toward the composition axis and rises steeply to the composition ordinate for 65% strontium nitrate. Adding more strontium results in decomposition of the

TABLE 3

(Transition Point: 252.5°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals	Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals
1	0	80	20	285°	10	30	56	14	326°
2	5	76	19	276	11	35	52	13	350
3	10	72	18	265	12	40	48	12	380
4	15	68	17	257	13	45	44	11	404
5	17.5	66	16.5	252.5	14	50	40	10	428
6	19	64.8	16.2	259	15	55	36	9	452
7	20	64	16	266	16	60	32	8	476
8	22.5	62	15.5	282	17	65	28	7	497
9	25	60	15	298					

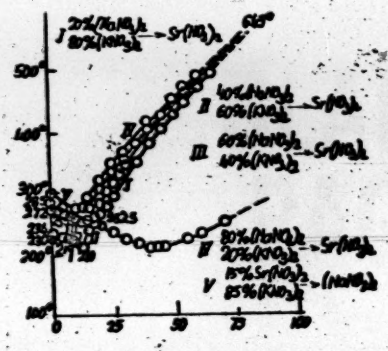


Fig. 3.

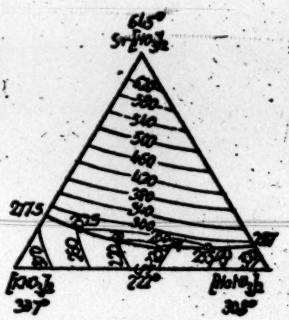


Fig. 4.

TABLE 4

(Transition Point: 210°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals	Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals
1	0	60	40	234°	10	27.5	43.5	29	340
2	5	57	38	228	11	30	42	28	350
3	10	54	36	216	12	35	39	26	370
4	12.5	52.5	35	210	13	40	36	24	394
5	15	51	34	237	14	45	33	22	421
6	17.5	49.5	33	260	15	50	30	20	443
7	20	48	32	282	16	55	27	18	465
8	22.5	46.5	31	302	17	60	24	16	490
9	25	45	30	312					

salts. The transition point is located at 210° and a composition of 12.5% strontium nitrate, 52.5% potassium nitrate, and 35% sodium nitrate (Fig. 3 and Table 4).

Section III: 60% $(NaNO_3)_2$ + 40% $(KNO_3)_2 \rightarrow Sr(NO_3)_2$, has two crystallization branches: a short branch for the crystallization of solid solutions of potassium and sodium nitrates, which drops almost rectilinearly to the transition point, and a branch for the crystallization of strontium nitrate, which rises steeply to the composition ordinate for 60% strontium nitrate. The transition point is located at 219° and a composition of 9% strontium nitrate, 35.5% potassium nitrate, and 55.5% sodium nitrate. The melting points of the melts have been traced as high as 491° along the sectional line III. Decomposition of the salts sets in above that temperature (Fig. 3 and Table 5).

TABLE 5
(Transition Point 219°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals	Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals
1	0	40	60	230°	10	25	30	45	333°
2	2.5	38.5	59	228	11	30	28	42	353
3	5	37.5	57.5	225	12	35	26	39	382
4	7.5	36	56.5	223	13	40	24	36	404
5	9	35.5	55.5	219	14	45	22	33	427
6	10	35.2	54.8	224	15	50	20	30	448
7	12.5	35	52.5	252	16	55	18	27	470
8	15	34	51	277	17	60	16	24	491
9	20	32	48	307					

Section IV: 80% $(NaNO_3)_2$ + 20% $(KNO_3)_2 \rightarrow Sr(NO_3)_2$, has two crystallization branches: a short one for the crystallization of solid solutions of potassium and sodium nitrates, which is slightly convex toward the composition axis, and a long one for the crystallization of strontium nitrate, which rises steeply to the composition ordinate for 60% strontium nitrate. The transition point is located at 255.5° and a composition of 10% strontium nitrate, 18.5% potassium nitrate, and 71.5% sodium nitrate. The melting points of the melts have been traced up to 495° along the sectional line IV, the molten mass decomposing above that temperature (Fig. 3 and Table 6).

TABLE 6
(Transition Point 255.5°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals	Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals
1	0	20	80	272°	9	15	17	68	296°
2	2.5	19.5	78	270	10	20	16	64	325
3	5	19	76	267	11	25	15	60	345
4	7.5	18.7	73.8	262	12	30	14	56	370
5	10	18.5	71.5	255.5	13	40	12	48	415
6	11	18.2	70.8	262	14	50	10	40	453
7	12	18	70	270	15	60	8	32	495
8	13	17.5	69.5	277					

Section V: 15% $Sr(NO_3)_2$ + 85% $(KNO_3)_2$ → $(NaNO_3)_2$, was drawn to determine whether the solid solutions break down into separate crystallization regions for the sodium and potassium nitrates. In contrast to the Sections I, II, III, and IV described above, Section V is a continuous curve with a minimum at 212° and a composition of 8.5% strontium nitrate, 49% potassium nitrate, and 42.5% sodium nitrate (Fig. 3 and Table 7).

TABLE 7

(Minimum at 212°)

Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals	Point No.	Equimolecular per cent $Sr(NO_3)_2$	$(KNO_3)_2$	$(NaNO_3)_2$	Temp. first crystals
1	15	85	0	302°	9	9	51	40	213°
2	14	81	5	289	10	8.5	49	42.5	212
3	13.5	76.5	10	277	11	8	47	45	214
4	13	72	15	262	12	7.5	42.5	50	216
5	12	68	20	250	13	7	38	55	224
6	11	64	25	237	14	6	34	60	235
7	10.5	59.5	30	224	15	4.5	25.5	70	252
8	10	55	35	215					

As we see from Fig. 3, the fusibility curve for Section V is typical of those cases in which the components form a continuous series of solid solutions with one another. There are no signs of any decomposition of the solid solutions along Section V, which was investigated up to the composition ordinate for 70% sodium nitrate, as it was impossible to determine the melting points above that composition.

The nature of the binary systems that are the primary constituents of the ternary system: strontium nitrate – potassium nitrate and strontium nitrate – sodium nitrate, served as a basis for the theoretical forecast of a fusibility diagram with a single eutectic point and separate crystallization areas of its constituents. The fusibility diagram of the ternary system, plotted from the foregoing experimental data, displayed a line of joint crystallization, however, with a minimum located at 308° and a composition of 11.3% strontium nitrate, 45% sodium nitrate, and 44.7% potassium nitrate, and with two crystallization areas: a strontium nitrate area with a crystallization surface at 77.18% and an area for the isomorphic mixture of potassium and sodium nitrates, which does not undergo decomposition. The crystallization surface of the isomerphic mixture was 22.82%.

The results of our experimental study of the ternary system have been summarized in the triangular projection of the isotherms of the three-dimensional phase diagram (Fig. 4). Figure 5 is an orthogonal projection of the crystallization path on the potassium nitrate–sodium nitrate side of the triangle. The singularity of the system investigated is readily seen in the crystallization curve.

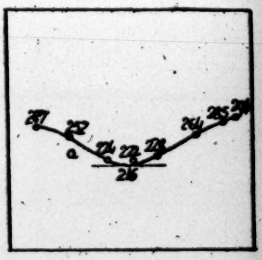


Fig. 5.

The curve of joint crystallization of the three components is bent, with a minimum, as is characteristic of solid solutions. The joint crystallization curve demarcates only two areas: a large area of pure strontium nitrate, and an area of isomorphic crystals of KNO_3 + $NaNO_3$. A general view of the fusibility diagram of the ternary system is given in the photograph of the model (Fig. 6: see Plate, page 1699)*.

SUMMARY

1. The visual-polythermal method of physicochemical analysis has been used in a study of the ternary system consisting of the nitrates of strontium, potassium, and sodium.

2. The following binary systems have been investigated:

a) Strontium nitrate – sodium nitrate, which has a eutectic with a melting point of 287° and a composition of 9.5 equimolecular per cent of strontium nitrate and 90.5 equimolecular per cent of sodium nitrate.

b) Strontium nitrate – potassium nitrate, which has a eutectic with a melting point of 278° and a composition of 25 equimolecular per cent of strontium nitrate and 75 equimolecular per cent of potassium nitrate.

3. It has been found that the fusibility of the ternary system constituted by the nitrates of strontium, potassium, and sodium is that of systems possessing a minimum. This minimum is located at 208° and a composition of 10.3 equimolecular per cent of strontium nitrate, 45 equimolecular per cent of sodium nitrate, and 44.7 equimolecular per cent of potassium nitrate.

The line of the joint crystallization of the three constituents divides the fusibility diagram of the ternary system into 2 regions: the strontium nitrate region with a crystallization surface of 77.18 equimolecular per cent, and the region of solid solutions of potassium and sodium nitrate, with a crystallization surface of 22.82 equimolecular per cent.

4. In the ternary system, the strontium nitrate, as the component whose melting point is higher than those of the components that form solid solutions, not only does not cause the solid solutions to decompose, but is actually a stabilizing factor.

LITERATURE CITED

[1] A.G.Bergman, Bull. USSR Acad. Sci., Div. Chem. Sci., 14, 97 (1941).

[2] Landolt-Börnstein. Physikalisch-Chemische Tabellen I, II, III, Berlin (1923, 27, 31).

[3] Handbook of Physical and Chemical Constants, p. 143-192. Moscow (1930).

[4] Ibid, 7, 190-201, Moscow, (1930).

[5] J.Dans and Lax. Taschenbuch fur Chemiker und Physiker, 235, Berlin. (1943).

[6] A.P.Palkin, J.Russ.Phys.Chem. Soc. 59, 1334 (1927).

[7] A.P.Palkin, J.Russ.Phys.Chem.Soc., 60, 317 (1928).

[8] N.A.Dailidovich, and M.A.Nikitin, Sci. Rep. Rostov State University Trans. Faculty of Chemistry III, 28-31 (1941).

[9] P.I. Protsenko and A.G.Bergman, J.Gen.Chem. 20, 1366 (1950).

Received October 10, 1949.

Chair of General and Inorganic Chemistry
Rostov-on-Don State University.

* See C.B.Translation, p. 1421.

PHYSICOCHEMICAL INVESTIGATIONS OF CONCENTRATED SOLUTIONS

XI. THE $SbBr_3 \cdot AlBr_3$ – CBr_4 SYSTEM

A. Ya. Gorenbein and E. E. Kriss

In previous reports one of the present authors has shown [1] that applying a viscosity correction causes the maximum of the molar conductance of systems consisting of an electrolyte and a dielectric (the solvent) to vanish, so that the molar conductance, corrected for viscosity, rises uniformly with increasing concentration of the electrolyte. As we see it, this rise in the corrected molar conductance with increasing electrolyte concentration ought to hold good up to the ultimate concentration of the electrolyte, i.e., the individual electrolyte, existing in the liquid state without any solvent at the same temperature at which the solution was tested. The correctness of this assertion has been proved in systems consisting of coordination compounds of aluminum bromide and bromides of various metals, with aluminum bromide as the solvent [2].

The difficulties involved in checking this assumption arise from the circumstance that the boiling point of the solvents is usually lower than the melting points of the salts. Therefore, bearing in mind that: 1) the components of the coordination compound $SbBr_3 \cdot AlBr_3$ do not constitute conducting solutions with CBr_4; 2) the thermal analysis findings indicate that aluminum bromide does not form a chemical compound with CBr_4 [3]; and 3) the melting point of carbon tetrabromide is higher than that of the coordination compound $SbBr_3 \cdot AlBr_3$, we decided to make a study of the $SbBr_3 \cdot AlBr_3$ – CBr_4 system in order to check the effect of viscosity on the molar conductance, on the one hand, and on the other, to investigate the change in the $\mu \cdot \eta$ product with dilution, starting with the individual electrolyte, $SbBr_3 \cdot AlBr_3$, at various temperatures.

Initial substances and experimental procedure. The aluminum bromide and antimony bromide were prepared as described in a report by one of the present authors [4]. The carbon tetrabromide was prepared and purified by the method described by Bartal [5], involving its synthesis from acetone and bromine in an alkaline medium, followed by repeated recrystallization of the resultant CBr_4 from methanol and its desiccation with P_2O_5.

The procedure used in preparing the solutions and the measurement technique have been described in a paper by one of the present authors [6]. The $SbBr_3 \cdot AlBr_3$ was melted in CBr_4 by slowly heating the two at as low a temperature as possible over an oil bath in order to avoid any eventual decomposition of the carbon tetrabromide.

The usual cell with a ground-glass stopper was used in measuring the conductance. The electrodes were not platinized (the platinizing came off in the molten masses). The cell constants of the cells we used ranged from 0.096 to 0.2863).

It should be said that the color of the solutions varied from crimson to a deep, dark red, depending upon the electrolyte concentration employed. This was due, apparently to a certain amount of decomposition of the CBr_4.

Experimental. According to the thermal analysis findings, antimony bromide forms a coordination compound $SbBr_3 \cdot AlBr_3$ [3], which is a good conductor in the molten state, with aluminum bromide. Hence, the $SbBr_3 \cdot AlBr_3 - CBr_4$ system may be regarded as a binary one in which the electrolyte is the $SbBr_3 \cdot AlBr_3$.

Since we were interested in the effect of dilution upon the corrected molar conductance, beginning with the individual electrolyte, we investigated the conductance, the viscosity, and the specific gravity at the higher concentrations. Our measurement results are listed in Tables 1-4, $d^t/4°$ being the specific gravity; κ the specific conductance, φ the dilution (in ml), μ the molar conductance, η the viscosity, and $\mu \cdot \eta$ the product of the molar conductance and the viscosity.

TABLE 1

$SbBr_3 \cdot AlBr_3 - CBr_4$ System at 85°

Weight % $SbBr_3 \cdot AlBr_3$	$d^t/4°$	$\kappa \cdot 10^3$	φ	μ	$\eta \cdot 10^2$	$\mu \cdot \eta$
50.5	3.131	2.47	397.7	0.98	4.766	0.047
54.4	3.145	3.12	367.4	1.15	5.42*	0.062
60.7	3.175	4.12	325.8	1.34	6.422	0.086
79.2	3.256	6.62	243.7	1.61	11.601	0.187
87.6	3.283	7.51	217.8	1.63	15.315	0.250
89.9	3.305	7.78	211.0	1.64	16.233	0.266
92.5	3.317	-	-	-	18.055	-
95.0	3.324	8.10	199.0	1.61	19.704	0.317
100.0	3.346	8.43	187.7	1.58	23.466	0.371

TABLE 2

$SbBr_3 \cdot AlBr_3 - CBr_4$ System at 90°

Weight % $SbBr_3 \cdot AlBr_3$	$d^t/4°$	$\kappa \cdot 10^3$	φ	μ	$\eta \cdot 10^2$	$\mu \cdot \eta$
50.5	3.118	2.68	339.2	1.07	4.283	0.046
54.4	3.133	3.40	368.9	1.25	4.85*	0.061
60.7	3.162	4.51	327.1	1.47	5.614	0.082
79.2	3.244	7.30	244.6	1.78	9.949	0.177
87.6	3.279	8.30	218.7	1.81	12.924	0.234
89.9	3.292	8.60	212.3	1.82	13.637	0.248
92.5	3.306	-	-	-	15.174	-
95.0	3.313	9.00	199.7	1.80	16.527	0.297
100.0	3.335	9.39	188.3	1.77	19.561	0.346

Figures 1 and 2 show the variation of the specific conductance and the viscosity, respectively, with concentration and temperature. As the concentration rises, the specific conductance increases, while it drops with increasing temperature. The isotherms of specific conductance are concave upward. As we see in the curves of Fig. 2, the viscosity increases with concentration, slowly at first and then more rapidly. Raising the temperature diminishes the viscosity

* The figures marked with an asterisk were found by interpolation.

TABLE 3

$SbBr_3 \cdot AlBr_3 - CBr_4$ System at 95°

Weight % $SbBr_3 \cdot AlBr_3$	$d^t/4°$	$\kappa \cdot 10^3$	φ	μ	$\eta \cdot 10^2$	$\mu \cdot \eta$
50.5	3.106	2.89	400.8	1.16	3.899	0.045
54.4	3.120	3.68	370.3	1.36	4.32	0.059
60.7	3.152	4.88	328.2	1.60	5.042	0.081
79.2	3.231	7.94	245.6	1.95	8.735	0.170
87.6	3.267	9.11	219.0	1.99	11.299	0.225
89.9	3.281	9.40	213.0	2.00	11.688	0.234
92.5	3.294	-	-	-	13.048	-
95.0	3.301	9.91	200.3	1.98	14.077	0.279
100.0	3.322	10.34	189.1	1.95	16.399	0.320

TABLE 4

$SbBr_3 \cdot AlBr_3 - CBr_4$ System at 100°

Weight % $SbBr_3 \cdot AlBr_3$	$d^t/4°$	$\kappa \cdot 10^3$	φ	μ	$\eta \cdot 10^2$	$\mu \cdot \eta$
50.5	3.094	3.16	402.5	1.27	3.527	0.045
54.4	3.108	4.01	371.8	1.49	3.92	0.058
60.7	3.135	5.30	330.0	1.75	4.539	0.079
79.2	3.218	8.84	246.6	2.18	7.698	0.161
87.6	3.258	10.20	220.0	2.24	9.655	0.216
89.9	3.270	10.50	214.0	2.25	10.192	0.229
92.5	3.281	-	-	-	11.292	-
95.0	3.291	11.13	201.0	2.24	12.091	0.271
100.0	3.313	11.64	189.6	2,21	13.957	0.308

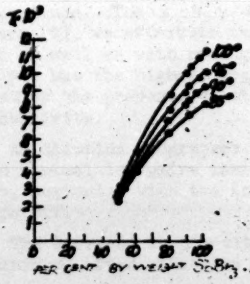


Fig. 1. Isotherms of specific conductance for the $SbBr_3 \cdot AlBr_3 - CBr_4$ system.

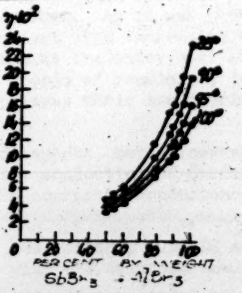


Fig. 2. Viscosity isotherms for the $SbBr_3 \cdot AlBr_3 - CBr_4$ system.

of the system. The curves are all concave upward. The curves in Fig. 3 represent the variation of the molar conductance and of the product of molar conductance times viscosity with dilution. As the concentration is raised, the

molar conductance increases at first to a maximum and then drops off. When allowance for viscosity is made, the maximum on the molar conductance curve vanishes, the $\mu \cdot \eta$ product rising as the $SbBr_3$-$AlBr_3$ concentration is increased and reaching its highest value for the pure $SbBr_3 \cdot AlBr_3$ electrolyte.

In this system as well, therefore, the appearance of a maximum on the molar conductance curve is due to the great increase in the system's viscosity as the electrolyte concentration is raised.

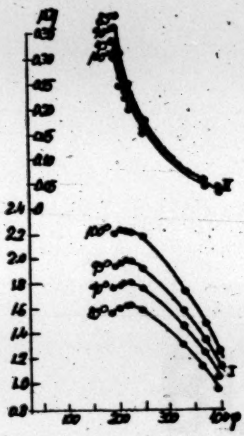


Fig. 3. Isotherms of molar conductance (I) and corrected molar conductance (II) for the $SbBr_3 \cdot AlBr_3$ – CBr_4 system.

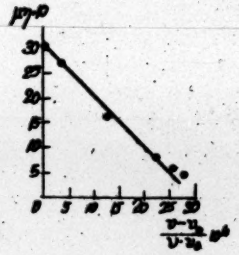


Fig. 4. Variation of the corrected molar conductance with the ratio $\frac{v - v_0}{v \cdot v_0}$.

The II curves in Fig. 3 denote the variation of $\mu \cdot \eta$ with dilution and temperature. The $\mu \cdot \eta - \varphi$ isotherms are close together. As in our previous papers [7], we attribute the decrease in the $\mu \cdot \eta$ product with increasing dilution as well as with rising temperature to the fact that the individual electrolyte has the highest degree of regularity. The degree of regularity is governed by the presence of structural groups, which possess their own intrinsic conductivity.

As dilution progresses, the structural groups disappear, being converted into neutral ion-pairs that do not participate in the conducting of current, so that, beginning with the individual electrolyte, the corrected conductance drops off.

The decrease in $\mu \cdot \eta$ with dilution in solutions possessing a high D_k attains a minimum, after which the $\mu \cdot \eta$ rises in accordance with the dilution law.

One feature of this system is that we were able to trace the effect of dilution, starting with the individual electrolyte, at four different temperatures. The isotherms II in Fig. 3. indicate that at high concentrations the $\mu \cdot \eta$ product drops off with rising temperature at any given concentration. We believe that this drop of the $\mu \cdot \eta$ product is due to the same causes that produce the decrease in the $\mu \cdot \eta$ product with dilution, i.e., the impairment of the regularity of the electrolyte with rising temperature.

The findings of the present research therefore fully bear out the concepts

developed previously concerning the nature of concentrated solutions [1,7].

One of the present authors has proposed that the variation of the corrected anomalous molar conductance with dilution at high concentrations be expressed by the equation:

$$\mu_1 = \mu_0 - k\frac{v - v_0}{v \cdot v_0},$$

where μ_0 is the corrected molar conductance of the individual electrolyte in the liquid state; v_0 is the volume of one mole of the electrolyte, in liters; μ_1 is the corrected molar conductance at the given dilution v; and k is a constant.

This equation may also be written thus:

$$\mu\eta = \mu_0\eta_0 - k_1\frac{v - v_0}{v \cdot v_0},$$

and ought to be represented by a straight line graphically.

To test this equation, we plotted the curve of $\mu\eta - [(v - v_0)/(v \cdot v_0)]$ for the one temperature of 100° (Fig. 4).

TABLE 5

$\mu \cdot \eta$	$\frac{v - v_0}{v \cdot v_0} \cdot 10^3$	$\mu \cdot \eta$	$\frac{v - v_0}{v \cdot v_0} \cdot 10^3$
0.045	2.790	0.216	0.731
0.058	2.585	0.228	0.595
0.079	2.244	0.271	0.299
0.161	1.220	0.308	0

Table 5 gives the numerical values of the $\mu \cdot \eta$ product and $(v - v_0)/(v \cdot v_0)$ at 100°.

As we see, the curve in Fig. 4 actually is a straight line for the concentration range from 100 to 60% $SbBr_3 \cdot AlBr_3$, which agrees with the formula cited above.

SUMMARY

1. The conductance, viscosity, and specific gravity of the $SbBr_3 \cdot AlBr_3 - CBr_4$ system have been investigated at 85, 90, 95, and 100° in the concentration range of 50-100% $SbBr_3 \cdot AlBr_3$.

2. It has been shown that appearance of a maximum on the molar conductance curve is due to the increased viscosity of the system as the concentration of the $SbBr_3 \cdot AlBr_3$ electrolyte is raised.

3. It has been found that the $\mu \cdot \eta - \varphi$ curves are anomalous, the variation of $\mu \cdot \eta$ with dilution being expressed satisfactorily by the equation:

$$\mu \cdot \eta = \mu_0\eta_0 - k_1\frac{v - v_0}{v \cdot v_0}$$

for the 100-60% $SbBr_3 \cdot AlBr_3$ concentration range.

4. It has been found that the maximum corrected molar conductance of the system corresponds to the corrected conductance of the individual electrolyte.

LITERATURE CITED

[1] E.Ya.Gorenbein, Proc. Inst. Chem., Ukrain. Acad. Sci., 7, 213 (1940); E.Ya.Gorenbein and G.A.Ridler, J.Gen.Chem. 11, 1069 (1941); E.Ya.Gorenbein, J. Phys. Chem. 18, 518 (1944); J.Gen.Chem. 15, 729 (1945); J.Gen.Chem. 17, 873 (1947); J.Phys.Chem. 20, 881 (1946).

[2] E.Ya.Gorenbein, J.Gen.Chem., 15, 729 (1945); 17, 873 (1947).

[3] V.A.Izbekov, Z. allg. anorg. Chem., 143, 80 (1925).

[4] E.Ya.Gorenbein, J.Gen.Chem. 18, 1427 (1948).

[5] A.Bartal, Chem. Ztg., 29, 377 (1905).

[6] E.Ya.Gorenbein, Proc. Inst. Chem., Ukrain. Acad. Sci., 7, 213 (1940).

[7] E.Ya.Gorenbein, J.Phys.Chem. 20, 881 (1946); J.Gen.Chem. 17, 873 (1947); 18, 1427 (1948).

Received September 26, 1949

Laboratory of Nonaqueous Solutions,
Institute of General and Inorganic Chemistry
Ukrainian Academy of Sciences

TABLE OF THE D. I. MENDELEEV PERIODIC SYSTEM OF CHEMICAL ELEMENTS, BASED ON THE ELECTRONIC STRUCTURE OF ATOMS

V. L. Albansky

D.I.Mendeleev was convinced that "the periodic variability of simple and complex bodies obeys some higher law, the nature and cause of which there is as yet no means of encompassing" [1]. At the present time science possesses this 'higher law', and the latter has become the foundation for arranging the elements in a table according to two new characteristics: 1) the charge on the nucleus or, which amounts to the same thing, the atomic number of the element; and 2) the electronic structure of the atom. The charge on the neucleus faultlessly established the order of the elements, which coincides perfectly with the sequence established by D.I.Mendeleev; the atom's electronic structure, explaining the periodicity in the elements' properties, indicates their places in the several groups. The periodic law, which was the basis for later achievements in the exploration of atomic structure, was itself corroborated anew by these discoveries.

When D.I.Mendeleev said that 'Apparently, the periodic law is not threat ened with demolition in the future, only extension and development lying ahead of it" [2], he foresaw that there would be "additions" to the periodic table of the chemical elements. More than one hundred tables have been published here and abroad by now, endeavoring to convey the best representation of the achievements of science in atomic structure.

The principal objectives confronting the authors of these tables were: 1) to link the entire table via one common idea, governing the distribution of all the elements; 2) to select the form for the table; 3) to fix the position of hydrogen; 4) to determine the position of helium and the other inert gases; 5) to place the lanthanoids and the actinoids; 6) to designate the subgroups; 7) to include the quantum shell numbers; 8) to denote the transition of s electrons to the d state, as is observed in dozens of elements; and 9) lastly, the table must not only be based upon the electronic structure of the atoms, but also make it possible to plot atomic structure easily.

The present author has solved these problems in the following manner:

1) The elements are arranged in sequence according to their atomic number and arranged in groups according to the electronic structure. 2) the form of the table, set up with the periods as the horizontal rows, is the short form, i.e., with paired periods, beginning with Period IV. This was the form of table preferred by D.I.Mendeleev; it is widely accepted, represents the intermittent development of the elements, and indicates the resemblances between such elements as chlorine and manganese, which display this resemblance in their higher oxides and fall into different subgroups of the same group. 3) Hydrogen, having one s' electron, is placed in Group I, where it heads an entire subgroup of elements having s' electrons, in which the ionization potential decreases

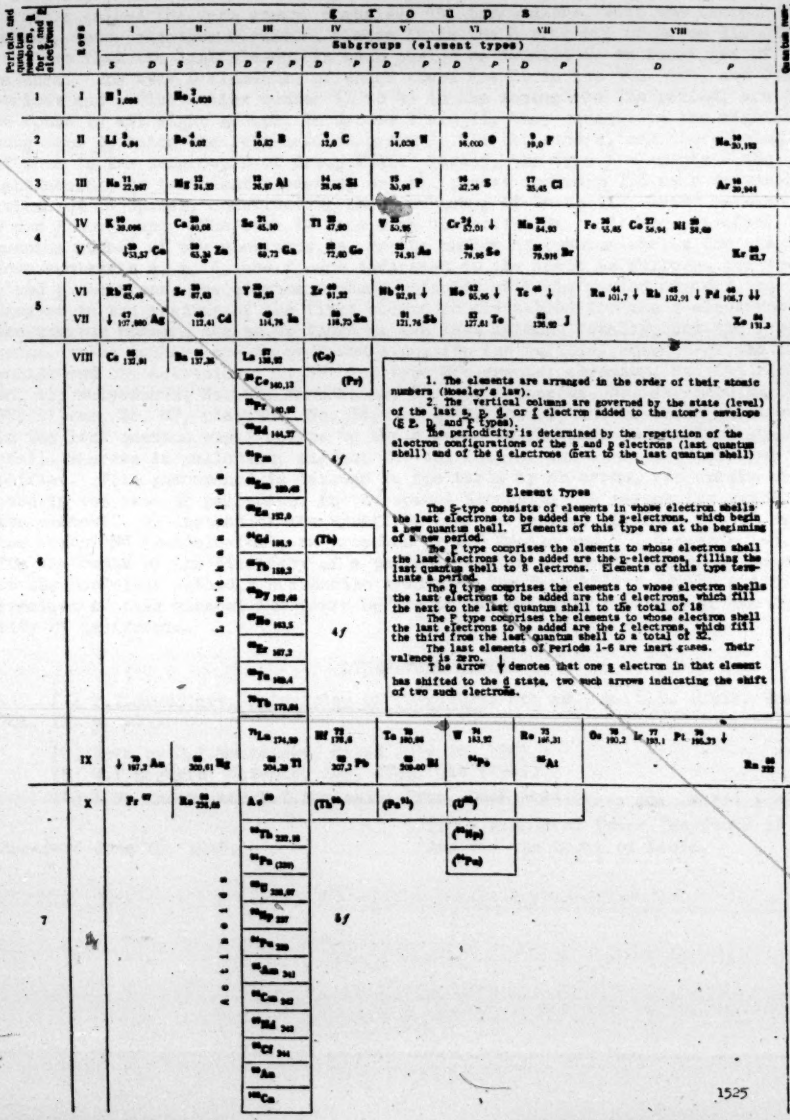
from hydrogen to cesium, as it should. 4) Helium, which has a second s electron, is placed in Group II, in the subgroup of the alkali earth elements. Its position in this subgroup is also borne out by the fact that helium has a spectrum like the spectra of other elements in this subgroup. The other inert gases, which possess six p electrons, are placed in Group VIII. The zero valence of the inert gases should be expressed by the following: elements that complete the six full periods have a stable electronic shell (2 electrons in the first period and 8 in all the others) and zero valence, and are inert gases. 5) The lanthanoids are covered by the table, constituting a third middle subgroup in Group III arranged as a vertical column of 14 spaces underneath lanthanum. They are all tervalent, three of them being also tetravalent, in addition. The last electron of each of these elements is added to the 4th quantum shell (the third from the last), filling it up progressively to the total of 32. These electrons constitute a special subgroup and are called f electrons; they have no valence, i.e., adding them to the electronic sphere of an atom does not increase the valence of these elements.

The present author explains the higher valence (above three) of some of the lanthanoids and actinoids as follows. When the last electrons are added to the electron envelope of the atoms of these elements, the change in energy level is slight, owing to the closeness of sublevels 4f to 5d, and of 5f to 6d, as well as to their great distance from the center of the atom, no matter whether these electrons are in the 4f or 5d state in the lanthanoids or in the 5f or 6d state in the actinoids. As a result, the f electrons of these elements change their positions readily, from the f state to the d state and vice versa, this being done even more readily in many of the actinoid elements, inasmuch as the 5f and 6d sublevels in these elements are still farther from the atom center and closer to each other. In the d state these electrons are valence electrons and, hence, raise the valence of the elements: in the 6th period cerium, praseodymium, and terbium being raised to 4; and in the 7th period, thorium being raised to 4, protactinium to 5, and uranium, neptunium, and plutonium to 6. X-ray examination of Element No. 90, thorium, discloses no f electrons, whereas uranium, No. 92, already has 3 [3], i.e., the number required if the f shell began to fill up at thorium. In the lanthanoids, after the f electron of neodymium has been added to the atom's electron envelope, the last electrons of cerium and praseodymium occupy the f state permanently, the same being true of the f electron of terbium after the f electron of dysprosium has been added. It is harder to fix this boundary in the actinoids, inasmuch as, if it does exist at all, it is located among artificially produced elements, only little X-ray analysis of which has been accomplished as yet, but if we are to go by the higher oxidation states, namely, VI in plutonium and III in americium and curium, this boundary begins at americium.

Inasmuch as the arrangement of the elements in groups in the present paper is based upon their electronic structure, each of the lanthanoids and actinoids in which the f electron shifts to the d state and, hence, an element that can have a dual structure, occupies two spaces in the table, one among the F type of elements and the other among the D type, the element's symbol being enclosed in parentheses in the latter case. 6) A new feature of the proposed table is designation of the subgroups. The short form of table proved to be best suited for this purpose. The reasons why the author arrived at this conclusion are as follows. D.I.Mendeleev called the elements of two short periods typical ones. The author retains this term and includes in the S type those elements in which the last electrons to be added to their electron envelope are s electrons. Correspondingly, the Types P, D, and F comprise the elements in which the last electrons

D. I. MENDELEEV'S PERIODIC SYSTEM OF THE CHEMICAL ELEMENTS AS BASED ON THE ELEMENTS' ATOMIC NUMBER (NUCLEUS) AND ELECTRON CONFIGURATION (SHELL)

"Extended" By V. L. Albansky


Groups
Subgroups (element types)
Periods and quantum numbers, n, for n and ℓ electrons
Rows
Quantum number n for d
Actinides
Lanthanides
1. The elements are arranged in the order of their atomic numbers (Moseley's law).
2. The vertical columns are governed by the state (level) of the last s, p, d, or f electron added to the atom's envelope (S, P, D, and F types).
The periodicity is determined by the repetition of the electron configurations of the s and p electrons (last quantum shell) and of the d electrons (next to the last quantum shell)
Element Types
The S-type consists of elements in whose electron shells the last electrons to be added are the s-electrons, which begin a new quantum shell. Elements of this type are at the beginning of a new period.
The P type comprises the elements to whose electron shell the last electrons to be added are the p-electrons, filling the last quantum shell to 8 electrons. Elements of this type terminate a period.
The D type comprises the elements to whose electron shells the last electrons to be added are the d electrons, which fill the next to the last quantum shell to the total of 18
The F type comprises the elements to whose electron shell the last electrons to be added are the f electrons, which fill the third from the last quantum shell to a total of 32.
The last elements of Periods 1-6 are inert gases. Their valence is ZERO.
The arrow ↓ denotes that one s electron in that element has shifted to the d state, two such arrows indicating the shift of two such electrons.

added are p, d, and f electrons, respectively. The type S elements occupy the left subgroups of Groups I and II, so that these two subgroups may be called S subgroups. The electrons of these elements begin a new quantum shell, while the elements themselves start the next period. The type P elements occupy the right-hand subgroups of Groups III-VIII, so that these subgroups have been called P subgroups; these elements terminate a period. The P subgroup of Group VIII, formerly called the zero group, comprises the inert gases, with the exception of helium, whose electron structure places it in the S subgroup of Group II. This requires that the last element in each period be denoted as an inert gas of zero valence. The type D elements, of which there are 10 in the 4th, 5th, and 6th periods and a fluctuating number (1 to 4) in the incomplete 7th period, are to be found in all eight groups; in Groups I and II, they constitute the right-hand subgroups D, being the left-hand subgroup in all the others, and there being 3 of them in the subgroup D of Group VIII. Lastly, the type F elements – the lanthanoids, as tervalent elements, are all placed in Group III as a vertical column of 14 spaces, constituting the F subgroup of Group III, lying between the D and P subgroups. The same is done with the actinoids. 7) The principal quantum number of the electrons, n, or the number of quantum shells for the various sublevels s, p, d, and f, are indicated in the table as follows: for the s and p electrons, the quantum numbers coincide with the period numbers, as indicated in the heading of the first column in the table; for the d electrons, the quantum numbers are to be found in the last column; finally, for the f electrons, these numbers are to be found alongside the vertical columns of the lanthanoids and the actinoids. 8) In nine type D elements: chromium, No. 24; niobium, No. 41; molybdenum, No. 42; technetium, No. 43; ruthenium, No. 44; rhodium, No. 45; silver, No. 47; platinum, No. 78; and gold, No. 79, one of the s electrons in the last quantum shell shifts to the d state in the next to the last quantum shell, whereas in palladium, element No. 46, both of the electrons are thus shifted. This phenomenon is denoted in the table by an arrow, two arrows being used in the case of palladium, in the spaces alongside the respective symbol for the element. 9) Instead of the symbol Bk (for berkelium), Element No. 97 has the symbol Md (mendelevium), as proposed by A.P Znoiko and V.I.Semishin [4]. "On the basis of the discovery of a periodic system of atomic nuclei by means of the Mendeleev method," A.P.Znoiko predicted the feasibility of the artificial creation of this element two years before it was actually produced at the University of California.

LITERATURE CITED

[1] D.I.Mendeleev, Principles of Chemistry, 8th ed., p. 617. (Coll. Wks., Vol. II, p. 509).

[2] Note by D.I.Mendeleev, dated July 10, 1905.

[3] W.F.Meggers, Science, 105, 2733, 514 (1947).

[4] A.P. Znoiko and V.I.Semishin, Proc. USSR Acad.Sci., 74, 5, 917 (1950).

Received June 26, 1949.

The V.M.Molotov Power Institute of Moscow
Awarded the Order of Lenin

THE REDUCTION OF SILICOTUNGSTATES WITH HYDROGEN

II. The Reduction of Unsaturated Potassium Silicotungstages

E. A. Nikitina and A. S. Kokurina

In our preceding paper we reported the results of reducing cis-silicotungstic (henceforth denoted by s.t.) acid and its eight potassium salts. The present paper reports on the results of the hydrogen reduction of potassium-6 and -5 s.t. and of the hypothetical solid solutions [1] of potassium silico-11-tungstate and silico-12-tungstate.

The reduction with hydrogen was carried out as specified in our first report [2]; we analyzed the reduction products by means of chemical analysis of the leaching alkali, cryoscopically, and by X-ray phase analysis [3]. The first sample of a solid solution of the 12th and 11th series tested by us had the composition set forth in Table 1.

The results of reducing the salt are set forth in Table 2 and Fig. 1, as well as in the X-ray photos.

M.A.Vladimirova was kind enough to do the X-ray analysis.

As in the salts of cis-s.t. acid the decomposition of the bronzes was accompanied by discontinuous changes in the direction of the curve. The computations of the X-ray photos are given in Tables 3 and 4.

TABLE 1

Analysis of the Salt

Chemical compound	Per cent found	Per cent in terms of anhydrous salt	Calculated from formula $4K_2O \cdot SiO_2 \cdot 11WO_3$
WO_3	79.93	85.77	85.36
SiO_2	1.79	1.92	2.01
K_2O	11.51	12.36	12.60
H_2O	6.81	-	-

TABLE 2

Reduction of the First Sample of Solid Solution

Temperature	Chemical analysis		X-ray analysis	Microscope findings
	Total K_2O, in %	K_2O leached out, %		
500°	12.38	5.71	Low intensity; lines blurred	Blue-gray powder with lustrous inclusions of faintly violet hue
600°	12.38	6.31	Intensive reflections from Pt-bronze; below-average intensity from W	Brown-gray conglomerates, all permeated with lustrous violet crystals.
700	12.38	11.28	Tungsten lattice predominates. 6 lines close to those of Pt-bronze	Gray powder with flashes of metallic tungsten

TABLE 3

Computation of X-Ray Photo of Sample I of Hypothetical Solid Solution, Reduced at 600°. Irradiation – Cu.

Line No.	Intensity	Observed $\sin^2\vartheta$	$\sin^2\vartheta$ of standard K-bronze	h, k, l for tungsten	$\sin^2\vartheta$, computed for tungsten
1	Average	0.0690	0.0688	–	–
2	Average	0.083	0.0825	–	–
3	Average	0.0912	0.0912	011β	0.102
4	Very strong	0.118	–	011α	0.119
5	Strong	0.143	–	–	–
6	Average	0.160	0.166	–	–
7	Average to weak	0.185	1.182	–	–
8	Strong	0.199	0.201	002β	0.204
9	Strong	0.235	0.235	002α	0.238
10	Strong	0.310	–	112β	0.310
11	Very strong	0.323	0.330	–	–
12	Average	0.353	0.360	112α	0.356
13	Average	0.370	–	–	–
14	Average	0.467	0.460	–	–
15	Very strong	0.486	–	022α	0.475
16	Strong	0.510	–	–	–
17	Blurred	0.550	0.550	–	–
18	Very strong	0.661	0.658	–	–
19	Very strong	0.632	0.698	–	–
20	Very strong	0.739	0.738	–	–
21	Very strong	0.834	–	–	–
22	Blurred	0.860	0.860	–	–
23	Very strong	0.880	–	–	–

TABLE 4

Computation of X-Ray Photo of Solid Solution Secured with Sample I, Reduced at 700°. Irradiation – Cu

Line No.	Intensity	Observed $\sin^2\vartheta$	$\sin^2\vartheta$ computed for K-bronze	h, k, l for tungsten	$\sin^2\vartheta$, computed for tungsten
1	Blurred	0.101	–	011β	0.102
2	Strong	0.120	–	011α	0.119
3	Weak	0.139	–	–	–
4	Average	0.240	–	002α	0.238
5	Very strong	0.294	0.294	–	–
6	Average	0.328	0.330	–	–
7	Very strong	0.357	0.360	112α	0.356
8	Weak	0.370	–	–	–
9	Average	0.473	0.460	022α	0.475
10	Average	0.490	–	–	–
11	Weak	0.508	–	–	–
12	Strong	0.585	0.580	–	–
13	Strong	0.676	–	–	–
14	Weak	0.713	–	222α	0.713
15	Weak	0.739	0.738	–	–
16	Very strong	0.827	–	123α	0.832

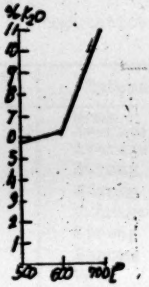


Fig. 1. Reduction of solid solution sample I.

Fig. 2. Reduction of solid solution sample II.

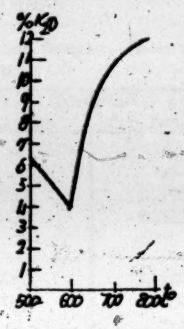


Fig. 3. Reduction of solid solution sample III.

The first column of the tables gives the numbers of the lines in sequence; the second column gives the observed visual intensity of blackness of the lines on the five-point system (very strong, strong, average, weak, very weak); the third column gives the values of the observed $\sin^2\vartheta$; the fourth column gives the same value computed for the standard potassium bronze; the fifth column gives the Miller indexes h, k, and l for metallic tungsten; and the sixth column gives the values of $\sin^2\vartheta$ computed for metallic tungsten.

TABLE 5

Chemical Composition of the Salt

Chemical compound	Per cent found	Per cent in terms of anhydrous salt	Calculated from formula $4K_2O \cdot SiO_2 \cdot 11WO_3$
WO_3	79.72	85.72	85.36
SiO_2	1.79	1.92	2.01
K_2O	11.41	12.27	12.60
H_2O	7.08	–	–

TABLE 6

Reduction of the Second Solid Solution Sample

Temperature	Chemical analysis: Total K_2O, in %	Chemical analysis: K_2O leached out, %	X-Ray analysis	Microscope findings
500°	12.27	6.38	Weak intensity; lines blurred	Blue-gray powder with white inclusions of undecomposed salt crystals
600°	12.27	6.48	Tungsten lines present; lines of K-bronze predominate	Brown-gray powder of violet hue. Some lustrous violet bronze crystals
700	12.27	10.55	Distinct tungsten lattice; many lines characteristic of the bronzes	Dark-gray powder. Violet bronze crystals encountered
800	12.27	12.09	Tungsten lines predominate. Lines close to those of the bronzes present	Light-gray caking pieces

TABLE 7

Computation of X-Ray Photo of the Second Solid Solution Sample, Reduced at 600°. Irradiation – Cu

Line No.	Intensity	Observed $\sin^2 \vartheta$	$\sin^2 \vartheta$ of standard K-bronze	h, k, l for tungsten	$\sin^2 \vartheta$ computed for tungsten
1	Weak Average	0.0675	0.0688	–	–
2	Average	0.0820	0.0825	–	–
3	Strong	0.0961	0.091	011β	0.102
4	Strong	0.114	–	011α	0.119
5	Average	0.143	–	–	–
6	Strong	0.164	0.166	–	–
7	Strong	0.200	0.201	002β	0.204
8	Weak	0.237	0.235	002α	0.238
9	Weak	0.262	–	–	–
10	Weak	0.288	0.294	–	–
11	Strong	0.310	–	112β	0.306
12	Average	0.354	0.300	112α	0.356
13	Strong	0.480	–	022α	0.475
14	Weak	0.510	–	–	–
15	Weak	0.650	0.645	–	–
16	Very strong	0.669	0.668	–	–
17	Average	0.692	0.698	–	–
18	Strong	0.738	0.738	–	–
19	Very strong	0.835	–	123α	0.832
20	Very strong	0.875	–	–	–

The second sample of the hypothetical solid solution to be reduced had the composition indicated by Table 5.

The results of reducing the sample are set forth in Table 6 and Fig. 2; it is worthy of note that the undecomposed salt is conserved even at 500°, while dehydration is not yet complete.

TABLE 8

Computation of the X-Ray Photo of the Second Solid Solution Sample, Reduced at 700°. Irradiation – Cu.

Line No.	Intensity	Observed $\sin^2 \vartheta$	$\sin^2 \vartheta$ of standard K-bronze	h, k, l for tungsten	$\sin^2 \vartheta$ computed for tungsten
1	Blurred	0.098	–	011β	0.102
2	Very strong	0.120	–	011α	0.119
3	Strong	0.158	0.166	–	–
4	Strong	0.199	0.201	–	–
5	Average	0.237	0.235	002	0.238
6	Strong	0.292	0.294	–	–
7	Weak	0.324	0.330	–	–
8	Strong	0.354	0.360	112α	0.356
9	Average	0.470	–	022α	0.475
10	Strong	0.590	–	013α	0.594
11	Average	0.672	0.668	–	–
12	Average	0.713	–	123β	0.716
13	Very strong	0.832	–	123α	0.832
14	Weak	0.863	0.860	–	–

The decomposition curve of the bronze is of the usual type for potassium s.t.

Tables 7, 8, and 9 reproduce the computations of the X-ray photos for the solid solution at the reduction temperature tested; the X-ray photos are also reproduced (See plate, page 1699)

The third sample of a solid solution of the 11th and 12th potassium s.t. reduced with hydrogen had the composition given in Table 10.

TABLE 9

Computation of the X-Ray Photo of the Second Solid Solution Sample, Reduced at 800°. Irradiation – Cu

Line No.	Intensity	Observed $\sin^2$	$\sin^2$ of standard K-bronze	h, k, l for tungsten	$\sin^2$ computed for tungsten
1	Very strong	0.122	–	011α	0.119
2	Weak	0.161	0.166	–	–
3	Weak	0.197	0.201	002β	0.204
4	Strong	0.238	–	002α	0.238
5	Average	0.293	0.294	–	–
6	Very strong	0.361	0.360	112α	0.356
7	Very strong	0.478	–	022α	0.475
8	Very strong	0.598	–	013α	0.594
9	Average	0.669	0.668	–	–
10	Average	0.714	–	222α	0.713
11	Very strong	0.838	–	123α	0.832
12	Average	0.860	0.860	–	–

The results of reduction are set forth in Table 11, Fig. 3, and the reproduced X-ray photos.

The computation of the X-ray photos is given in Tables 12 and 13.

The X-ray photos are reproduced (see Plate, page 1699)

Fig. 3 shows the discontinuous change in the course of the curve during the decomposition of the bronze, as was the case in the other tests.

TABLE 10

Chemical Composition of the Salt

Chemical compound	Per cent Found	Per cent in terms of anhydrous salt	Calculated from formula $4K_2O \cdot SiO_2 \cdot 11WO_3$
WO_3	79.86	85.67	85.36
SiO_2	1.86	1.99	2.01
K_2O	11.50	12.34	12.60
H_2O	6.77	–	–

The fourth sample of a solid solution was reduced at 600 and 700°. The results of analysis of the salt are given in Table 14.

We cite the results that are shown by the X-ray photos of the salt; the corresponding computations of the X-ray photos are given in Table 15 and 16. The fourth solid solution sample was analyzed only by the X-ray method.

We then investigated the reduction of the 5th and 6th potassium s.t., these samples being reduced at 500, 600, and 700°. We did not analyze the samples of the reduced salts by the X-ray method, nor did we analyze the leach alkali, but confined ourselves to microscopic examination in this instance, as the fasted method of getting a qualitative estimate of the reduction process. Microscopic examination indicated that the intensely violet crystals of the bronze

TABLE 11

Reduction of the Third Solid Solution Sample

Temperature	Chemical analysis		X-Ray analysis	Microscope findings
	Total K_2O, in %	K_2O leached out, %		
500°	12.34	6.21	Weak intensity, though the bronze lines can be discerned.	Blue-gray powder with white and light-violet inclusions.
600	12.34	3.98	All intense reflections from the potassium bronze. Reflection from the tungsten lattice weak.	Brown-gray powder with shining golden-yellow crystals of bronze scattered through the field.
700	12.34	10.65	The tungsten lattice predominates. Lines coinciding with the bronze lines are present.	Dark-gray powder. Lustrous violet crystals of bronze are encountered
800	12.34	12.02	—	Light-gray caking powder.

TABLE 12

Computation of the X-Ray Photo of the Third Solid Solution Sample, Reduced at 600°. Irradiation – Cu

Line No.	Intensity	Observed $\sin^2\vartheta$	$\sin^2\vartheta$ of standard K-bronze	h,k,l for tungsten	$\sin^2\vartheta$ computed for tungsten
1	Average	0.0636	0.0688	–	–
2	Blurred	0.0912	0.0912	–	–
3	Average	0.119	–	011α	0.119
4	Average	0.144	–	–	–
5	Average strong	0.166	0.166	–	–
6	Strong	0.200	0.201	002β	0.204
7	Strong	0.231	0.235	002α	0.238
8	Average	0.267	–	–	–
9	Strong	0.295	0.294	–	–
10	Strong	0.330	0.327	–	–
11	Average	0.359	0.360	112α	0.356
12	Average-blurred	0.456	0.460	–	–
13	Strong	0.486	–	022α	0.475
14	Weak	0.558	0.550	–	–
15	Average	0.580	0.580	–	–
16	Strong	0.670	0.668	–	–
17	Strongly blurred	0.695	0.698	–	–
18	Strong	0.736	0.738	–	–
19	Strong	0.832	–	123α	0.832
20	Strong	0.875	–	–	–
21	Strong	0.915	–	–	–

TABLE 13

Computation of the X-Ray Photo of the Third Solid Solution Sample, Reduced at 700°. Irradiation - Cu

Line No.	Intensity	Observed $\sin^2\vartheta$	$\sin^2\vartheta$ of standard K-bronze	h, k, l for tungsten	$\sin^2\vartheta$ computed for tungsten
1	Blurred	0.0975	-	011β	0.102
2	Very strong	0.123	-	011α	0.119
3	Weak	0.160	0.166	-	-
4	Average strong	0.243	-	002α	0.238
5	Strong	0.300	0.294	-	-
6	Average	0.309	-	112β	0.307
7	Strong	0.333	0.330	-	-
8	Very strong	0.361	-	112α	0.356
9	Weak	0.371	0.360	-	-
10	Weak	0.480	-	022α	0.475
11	Average strong	0.492	-	-	-
12	Average strong	0.520	-	-	-
13	Strong	0.600	-	013α	0.594
14	Strong	0.672	0.668	-	-
15	Average	0.700	0.698	222α	0.713
16	Weak	0.707	-	123β	-
17	Average	0.749	-	-	-
18	Very strong	0.832	-	123α	0.832
19	Strong	0.890	-	-	-

TABLE 14

Analysis of the salt

Chemical compound	Per cent found	Per cent in terms of anhydrous salt	Calculated from the formula $4K_2O \cdot SiO_2 \cdot 11WO_3$ (%)
WO_3	79.88	85.64	85.36
SiO_2	1.89	2.03	2.01
K_2O	11.50	12.33	12.60
H_2O	6.73	-	-

were encountered only at 600°, no bronzes being found in the samples reduced at 500 and 700°.

In the overwhelming majority of cases, the reduction of the hypothetical solid solutions of the 11th and 12 potassium s.t. sets in at 500°. A bronze is formed very slowly at this temperature, however; the X-ray photos of the samples tested were unclear, most of the lines being blurry, which indicated the absence of an ordered arrangement of the atoms in the crystal lattice and that the lattice was undergoing rearrangement. X-ray analysis indicated that most of the lines typical of the standard potassium bronze are observed in the potassium s.t. that are reduced at 600°; the X-ray photos of the solid solutions of the 11th and 12th potassium s.t. resembled the X-ray photos of the octasubstituted potassium cis-silicotungstate.

At 700°, the X-ray photos display distinct tungsten lines, together with the bronze lines, the intensity of the tungsten lines being much higher than that of the bronzes. Microscopic examination also shows that the formation of bronzes

TABLE 15

Computation of the X-Ray Photo of the Fourth Solid Solution Sample, Reduced at 600°. Irradiation – Cu

Line No.	Intensity	$\sin^2\vartheta$ of standard K-bronze	Observed $\sin^2\vartheta$	Line No.	Intensity	$\sin^2\vartheta$ of standard K-bronze	Observed $\sin^2\vartheta$
1	Average	–	0.06	10	Strong	0.360	0.362
2	Weak	0.068	0.068	11	Blurred	0.460	0.457
3	Average	0.082	0.0812	12	Blurred	0.550	0.549
4	Average	0.166	0.164	13	Blurred	0.618	0.619
5	Weak	0.182	0.180	14	Blurred	0.658	0.655
6	Strong	0.201	0.199	15	Blurred	0.668	0.671
7	Strong	0.255	0.239	16	Average	0.860	0.863
8	Very strong	0.294	0.290	17	Very strong	–	0.925
9	Blurred	0.332	0.330				

TABLE 16

Computation of the X-Ray Photo of the Fourth Solid Solution Sample, re Reduced at 700°. Irradiation – Cu

Line No.	Intensity	Observed $\sin^2\vartheta$	$\sin^2\vartheta$ of standard K-bronze	h, k, l for tungsten	$\sin^2\vartheta$ computed for tungsten
1	Strong	0.120	–	011α	0.119
2	Weak	0.142	–	–	–
3	Average	0.241	–	002α	0.238
4	Weak	0.296	0.294	–	–
5	Weak	0.330	0.330	–	–
6	Strong	0.356	0.360	112α	0.356
7	Average	0.473	–	022α	0.475
8	Strong	0.595	–	013α	0.594
9	Average	0.675	0.668	–	–
10	Average	0.713	–	222α	0.713
11	Average strong	0.744	0.738	–	–
12	Very strong	0.832	–	123α	0.832

attains a maximum at 600°. The production of bronzes as the result of the reduction of solid solutions of the 5th and 6th potassium cis-s.t. is highly important for the theory of structure of heteropoly acids, compelling us, as it does, to regard the presence of the WO_3 radicals within the inner sphere of these compounds as most highly probable.

SUMMARY

1. A study has been made of the reduction of some unsaturated potassium silico-tungstates by hydrogen.

2. In the solid solutions of 11th and 12th s.t., the most bronzes are formed at 600°; at 700°, the bronzes are partially reduced to metallic tungsten.

3. The 5th and 6th potassium s.t. form bronzes only at 600°, no traces of bronzes being found in the samples tested at 500 or 700°.

4. The feasibility of producing bronzes from the potassium silicotung-

states from the 12th to the 5th series bears out the general pattern of the heteropoly acids based on coordination theory.

LITERATURE CITED

[1] E.A.Nikitina and A.S.Kokurina, J.Gen.Chem. 19, 967 (1949).*

[2] E.A.Nikitina and A.S.Kokurina, J.Gen.Chem 20, 1380 (1950).**

[3] E.A.Nikitina and A.S.Kokurina, J.Gen.Chem. 21, 1181 (1951):***

Received June 27, 1949

Laboratory of the Moscow Electric Lamp Factory

* See C. B. Translation, p. 957 ff.

** See C. B. Translation, p. 1437 ff.

*** See C.B. Translation.

THE SURFACE ENERGY OF MOLECULES AND THEIR PHYSICOCHEMICAL PROPERTIES

VI. Molecular Diameter, Surface Energy, and the Constant a in The Van Der Waal's Equation

S. G. Mokrushin

Some time ago the author [1] pointed out that the diameter of molecules could be calculated on the basis of Langmuir's assumption [2] of the existence of surface energy in individual molecules and assuming, as a first approximation, that the molecules are spherical. Subsequently, the author [3], making use of Langmuir's principle of independent surface action [4], suggested a number of equations for the variation of the boiling point of homologous compounds with the number of carbon atoms or of homologous groups.

In the present paper the author takes the surface energy of a liquid to be the work of drawing molecules into the liquid, in accordance with the views put forward by Adam [5]. This work of drawing molecules within a liquid is nothing but the work of the binding or internal pressure forces. In his well-known equation, van der Waals expresses the internal-pressure forces in a liquid by the term a/v^2, where a is a constant indicating the binding force, and v is the molar volume of the liquid. It may be concluded that the work necessary to disperse the liquid into isolated particles – drops equaling the individual molecule in size – will equal the work or energy required to overcome the internal-pressure forces when transforming one mole of the liquid into the gaseous state. This energy E_1 may be expressed by the equation:

$$E_1 = \int_{v_l}^{v_v} \frac{a}{v^2}\, dv = a\left(\frac{1}{v_l} - \frac{1}{v_v}\right), \qquad (1)$$

where a is the cohesion constant in the van der Waals equation, and v_l and v_v are the molar volumes of the liquid and the vapor. In dispersing the liquid to the molecular stage of dispersion, the resultant molecules of vapor will have the surface energy E_2, which can be expressed as the free surface energy per mole (Avrogadro number) of spherical molecules, i.e.:

$$E_2 = \gamma \pi d^2 N, \qquad (2)$$

where γ is the free surface energy, in ergs, per unit surface of the liquid.
d is the molecular diameter,
N is the Avogadro number ($6.06 \cdot 10^{23}$).

The two energy expressions, E_1 and E_2, are equal to each other, since they express the energy involved in the same process of dispersion or evaporation of the liquid. Hence, setting Equations (1) and (2) equal to each other, we get:

$$a\left|\frac{1}{v_l}-\frac{1}{v_v}\right| = \gamma\pi d^2 N. \qquad (3)$$

If Equation (3) is applied at temperatures that are far from the critical one (close to the melting point), the term $1/v_v$ may be neglected, compared to the $1/v_l$ term. We may therefore write Equation (3) as follows:

$$\frac{a}{v_l} = \gamma\pi d^2 N \qquad (4)$$

or

$$d = \sqrt{\frac{a}{v_l \cdot \gamma\pi N}} \qquad (5)$$

Equation (5) may be used to calculate the diameter of the molecules. If the constant a is expressed in liter-atm per mole, γ in ergs per sq cm, and v_l in liters per mole, and we bear in mind that 1 liter-atm equals $10.132 \cdot 10^8$ ergs, we get Equation (6), a form that is convenient for computation:

$$d = 2.307 \cdot 10^{-8}\sqrt{\frac{a}{v_l \gamma}}. \qquad (6)$$

Table 1 gives a series of calculated molecular diameters, based on the values of a, v_l, and γ found in the physicochemical handbooks [8].

TABLE 1

Substance	a, liter^2-atm/mole^2	γ ergs/sq cm.	$v_l \cdot 10^3$, liters/mole	molecular d, A°
He	0.0391	0.34	28.47	4.43
Ar	1.303	11.5	28.13	4.63
H_2	0.245	2.13	26.73	4.78
N_2	1.345	10.53	32.39	4.58
O_2	1.360	18.35	27.39	3.81
Cl_2	5.34	33.7	45.08	4.33
H_2O	5.47	75.0	18.0	4.64
$(CH_3)_2CO$	13.92	25.4	73.52	6.30

TABLE 2

Substance	Molecular diameter, Å			
	From the Sutherland gas velocity	From the van der Waals constant b	From the liquid volume at t and at a packing factor of 0.74	From Equation (6) and the van der Waals constant a
He	1.88	2.71	4.00; 271.5°	4.43
Ar	2.97	3.00	4.04; 189	4.63
H_2	2.39	2.81	3.99; 258	4.78
N_2	3.13	3.18	4.23; 202	4.58
O_2	2.96	3.00	3.88; 227	3.81

The molecular diameters calculated from Equation (6) and by other methods, according to Gertsfeld [7], are compared in Table 2.

We see from Table 2 that the molecular diameters calculated from Equation (6) are closest to those calculated from the liquid volume, on the assumption

that the liquid consists of close-packed molecular spheres, i.e., with a packing factor of 0.74. The molecular diameters calculated from Equation (6) are larger than those calculated from the equations of the kinetic theory of gases, since in the latter case the molecular diameters are determined from collisions between molecules. The higher the kinetic energy of the molecules, the more will the molecules be deformed at the instant of impact; thus, the kinetic diameter of the molecules will be the minimum distance between the centers of the spherical molecules at the instant of impact. As Lenard [8] has shown, this distance may be a thousand times smaller than the actual molecular diameter if the kinetic energy of the colliding molecules is high.

It follows that the molecular diameters found from Equation (6) are in agreement with the actual molecular diameter, provided the molecules are not deformed, but merely touch one another.

SUMMARY

1. It has been shown that the molecular diameters can be calculated on the assumption that molecules possess surface energy and by setting this energy equal to the free surface energy of the liquid, provided the process of molecular evaporation is regarded as a process of dispersing the liquid.

2. The work required for dispersion is taken to equal the energy consumed in opposing the binding forces (cohesion).

3. The binding forces are taken to equal the value of internal pressure in the van der Waals equation.

4. The molecular diameters calculated by this method are larger than those calculated from internal friction in gases; an explanation is supplied for this discrepancy.

LITERATURE CITED

[1] S.G.Mokrushin, J.Russ.Phys.Chem.Soc., 58, 491 (1926).

[2] J.Langmuir, J.Am.Chem.Soc., 39, 1848 (1917).

[3] S.G.Mokrushin, J.Gen.Chem. 1, 856 (1931); S.G.Mokrushin and E.I.Krylov, J.Gen.Chem. 2, 916 (1932); 3, 576 (1933).

[4] I.Langmuir, Colloid Symposium, Mon., 3, 48 (1925).

[5] N.K.Adam. The Physics and Chemistry of Surfaces (Russ. trans.), p. 12-16. (1947).

[6] Landolt-Börnstein. Physikalish-Chemischen Tabellen.

[7] Gertsfeld. The Kinetic Theory of Matter, p. 441-443. Moscow (1935).

[8] P.Lenard. Ueber Kathodenstrahlen, Nobel Vorlesung, Berth (1906).

Received October 23, 1949.

Laboratory of Physical and Colloid Chemistry
S.M.Kirov Urals Polytechnic Institute

THE POSITION OF THE MAXIMA ON THE OPTICAL DENSITY - COMPOSITION CURVE WHEN A SYSTEM'S CONCENTRATION IS BY THE ADDITION OF IONS

M. S. Marinov

In our first report we discussed the position of the maxima on the optical density – composition curves when a system's concentration is changed by adding substances that act as solvents in an investigation of cobalt halides. The present report discusses the case where lithium salts are employed as the third substance. In general, the composition of the system under test: cobalt perchlorate + a lithium halide + a third substance + a solvent, may be represented by a tetrahedron, the base of which is the triangle: cobalt perchlorate – lithium halide – third substance.

One of the sections of this tetrahedron may be explored to find the characteristics of the system. If the tetrahedron is cut by a plane parallel to its base at a point corresponding to a reagent concentration of 0.005 mole/liter, we get a triangle whose vertexes are located 0.005 mole/liter of the solutions of cobalt perchlorate, lithium halide, and the third substance. We explored three sections of this triangle, parallel to the cobalt perchlorate – lithium halide side, at the following concentrations of the third substance: $1.25 \cdot 10^{-3}$ mole/liter; $2.5 \cdot 10^{-3}$ mole/liter, and $3.75 \cdot 10^{-3}$ mole/liter.

Lithium perchlorate and lithium halides were utilized as the third substance. The lithium halides used as the third substance always had a different anion than the lithium halide located at one of the triangle vertexes along the cobalt perchlorate – lithium halide side.

The system solutions were prepared as follows. We began by preparing the following separate solutions: 1) 0.005 mole/liter of cobalt perchlorate; 2) 0.005 mole/liter of lithium halide; and 3) 0.005 mole/liter of the third substance.

The concentration ratios of the components of the cobalt perchlorate – lithium halide – third substance system in acetone are given in Tables 1, 2, and 3, while the corresponding ratios in ethyl alcohol are given in Tables 4 and 5. We also prepared the following isoconcentrates: the lithium perchlorate system $Co(ClO_4)_2 + LiCl + LiClO_4$ + acetone; the lithium bromide system $Co(ClO_4)_2 + LiCl +$ + LiBr + acetone; the lithium chloride system $Co(ClO_4)_2 + LiBr + LiCl$ + acetone; the lithium bromide system $Co(ClO_4)_2 + LiCl + LiBr$ + ethyl alcohol; and the lithium iodide system $Co(ClO_4)_2 + LiCl + LiI$ + ethyl alcohol. In preparing these mixtures, the 0.005 mole/liter solutions of cobalt perchlorate and the lithium halide were mixed together by the method of continuous changes [1].

The resulting solution mixtures had various proportions of cobalt perchlorate

TABLE 1

Isoconcentrates of Lithium Perchlorate: $Co(ClO_4)_2$ + LiCl + $LiClO_4$ in Acetone; Overall Concentration 0.005 mole/liter

Solution No.	Solution composition: Ml of solutions of $Co(ClO_4)_2$	Ml of solutions of LiCl	Concentration, mole/liter: $Co(ClO_4)_2$	Concentration, mole/liter: LiCl	D at λ (in mμ): 600	625	650	675	700
First lithium perchlorate isoconcentrate $[LiClO_4] = 1.25 \cdot 10^{-3}$ (2.5 ml solution)									
1	6.75	0.75	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.015	0.023	0.025	0.031	0.014
2	6.00	1.50	$3 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$	0.031	0.052	0.058	0.071	0.033
3	5.25	2.25	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.046	0.079	0.090	0.113	0.053
4	4.50	3.00	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.063	0.107	0.123	0.154	0.074
5	3.75	3.75	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.081	0.138	0.159	0.201	0.098
6	3.00	4.50	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.098	0.169	0.194	0.252	0.130
7	2.25	5.25	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.117	0.173	0.220	0.307	0.199
8	1.50	6.00	$7.5 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	0.098	0.096	0.159	0.274	0.292
9	0.75	6.75	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.046	0.071	0.091	0.155	0.174
Second lithium perchlorate isoconcentrate $[LiClO_4] = 2.5 \cdot 10^{-3}$ (5.0 ml solution)									
1	4.50	0.50	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.009	0.015	0.017	0.021	0.008
2	4.00	1.00	$2 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	0.021	0.035	0.039	0.047	0.022
3	3.50	1.50	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.031	0.053	0.059	0.076	0.035
4	3.00	2.00	$1.5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	0.040	0.072	0.082	0.109	0.049
5	2.50	2.50	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.054	0.096	0.109	0.137	0.065
6	2.00	3.00	$1 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.065	0.117	0.135	0.174	0.087
7	1.50	3.50	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.079	0.118	0.149	0.206	0.131
8	1.00	4.00	$5 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	0.065	0.059	0.101	0.198	0.189
9	0.50	4.50	$2.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.033	0.044	0.059	0.102	0.113
Third lithium perchlorate isoconcentrate $[LiClO_4] = 3.75 \cdot 10^{-3}$ (7.5 ml solution)									
1	2.25	0.25	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.007	0.011	0.010	0.012	0.005
2	2.00	0.50	$1 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.013	0.021	0.021	0.027	0.013
3	1.75	0.75	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.018	0.030	0.031	0.039	0.017
4	1.50	1.00	$7.5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	0.023	0.042	0.045	0.056	0.027
5	1.25	1.25	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.029	0.051	0.056	0.071	0.035
6	1.00	1.50	$5 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$	0.035	0.067	0.065	0.087	0.052
7	0.75	1.75	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.041	0.060	0.076	0.109	0.070
8	0.50	2.00	$2.5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	0.036	0.032	0.054	0.093	0.096
9	0.25	2.25	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.018	0.021	0.030	0.051	0.053

and lithium halide with constant volume and constant overall concentration, equaling 0.005 mole/liter. The total volume of the mixture of each solution of the isoconcentrates was 10 ml. For the initial isoconcentrates, 7.5 ml of a mixture of the cobalt perchlorate and lithium halide solutions was mixed with 2.5 ml of a 0.005 mole/liter solution of the third substance; for the second isoconcentrates 5 ml of a 0.005 mole/liter solution of the third substance was mixed with 5 ml of the mixed solutions of the cobalt perchlorate and the lithium halide; and for the third isoconcentrates 7.5 ml of a 0.005 mole/liter solution of the third substance was mixed with 2.5 ml of the mixed cobalt perchlorate and lithium halide solutions. The overall molar concentration of such a solution was 0.005 mole/liter. The technique of preparing the solution is seen in Table 1, which lists

TABLE 2

Isoconcentrates of Lithium Bromide: $Co(ClO_4)_2$ + LiCl + LiBr in Acetone: Overall Concentration 0.005 mole/liter

Solution No.	Solution composition Concentration (mole/liter)		D at λ (in mμ)					
	$Co(ClO_4)_2$	LiCl	600	625	650	675	700	725
First lithium bromide isoconcentrate [LiBr] = $1.25 \cdot 10^{-3}$ mole/liter								
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.124	0.169	0.201	0.222	0.098	0.022
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.154	0.215	0.254	0.278	0.124	0.027
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.179	0.250	0.294	0.325	0.147	0.033
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.208	0.295	0.350	0.389	0.182	0.043
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.243	0.335	0.403	0.455	0.230	0.058
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.269	0.330	0.422	0.515	0.343	0.107
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.243	0.201	0.325	0.485	0.470	0.163
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.144	0.144	0.223	0.343	0.325	0.087
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.065	0.088	0.117	0.184	0.177	0.038
Second lithium bromide isoconcentrate [LiBr] = $2.5 \cdot 10^{-3}$ mole/liter								
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.210	0.315	0.376	0.445	0.235	0.065
2	2.10^{-3}	5.10^{-4}	0.233	0.346	0.412	0.484	0.273	0.078
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.246	0.366	0.435	0.520	0.317	0.098
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.253	0.371	0.439	0.565	0.420	0.150
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.235	0.305	0.367	0.555	0.580	0.243
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.202	0.217	0.294	0.448	0.480	0.201
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.152	0.143	0.218	0.330	0.331	0.127
8	5.10^{-4}	2.10^{-3}	0.097	0.107	0.147	0.226	0.220	0.069
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.043	0.050	0.074	0.115	0.111	0.026
Third lithium bromide isoconcentrate [LiBr] = $3.75 \cdot 10^{-3}$ mole/liter								
1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.130	0.315	0.316	0.550	0.692	0.325
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.115	0.260	0.273	0.470	0.600	0.285
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.114	0.227	0.245	0.420	0.518	0.250
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.109	0.185	0.208	0.346	0.412	0.201
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.104	0.152	0.182	0.295	0.336	0.164
6	5.10^{-4}	$7.5 \cdot 10^{-4}$	0.091	0.118	0.146	0.230	0.250	0.118
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.076	0.083	0.115	0.175	0.186	0.085
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.054	0.056	0.077	0.121	0.124	0.052
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.025	0.026	0.038	0.058	0.058	0.019

the composition of the isoconcentrate solutions of lithium perchlorate. The optical density of the solutions was measured with a Beckmann photoelectric spectrophotometer.

Lithium perchlorate isoconcentrates of the $Co(ClO_4)_2$ + LiCl + $LiClO_4$ + acetone system. The lithium perchlorate preparation used was $LiClO_4 \cdot 3H_2O$, prepared as described in the literature [2]. The solutions were prepared as described above. The composition of the solutions and their optical density are given in Table 1.

As we see in Table 1, adding lithium perchlorate to the $Co(ClO_4)_2$ + LiCl + acetone system affects neither the position of the maxima on the optical density – composition curves nor the nature of the spectral absorption. All we find is a decrease in optical density. The third isoconcentrate solutions have lower

TABLE 3

Isoconcentrates of Lithium Chloride: $Co(ClO_4)_2$ + LiBr + LiCl in Acetone: Overall Concentration: 0.005 mole/liter

Solution No.	Solution composition Concentration (mole/liter) $Co(ClO_4)_2$	LiBr	D at λ (in mμ) 600	625	650	675	700	725
First lithium chloride isoconcentrate [LiCl] = $1.25 \cdot 10^{-3}$ moles/liter								
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.107	0.150	0.175	0.189	0.070	0.010
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.136	0.193	0.226	0.245	0.098	0.017
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.167	0.238	0.283	0.312	0.135	0.027
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.206	0.295	0.353	0.395	0.194	0.045
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.240	0.343	0.411	0.472	0.239	0.072
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.251	0.370	0.430	0.543	0.390	0.133
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.202	0.271	0.333	0.510	0.580	0.244
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.144	0.164	0.255	0.340	0.360	0.150
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-4}$	0.078	0.080	0.120	0.180	0.182	0.068
Second lithium chloride isoconcentrate [LiCl] = $2.5 \cdot 10^{-3}$ mole/liter								
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.180	0.260	0.305	0.343	0.138	0.025
2	2.10^{-3}	5.10^{-4}	0.210	0.295	0.350	0.398	0.175	0.037
3	$0.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.233	0.320	0.385	0.445	0.218	0.053
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.258	0.327	0.412	0.497	0.298	0.091
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.261	0.250	0.365	0.512	0.474	0.181
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.211	0.181	0.295	0.432	0.425	0.155
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.154	0.139	0.222	0.335	0.325	0.102
8	5.10^{-4}	2.10^{-3}	0.093	0.097	0.146	0.227	0.218	0.062
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.040	0.046	0.070	0.107	0.102	0.024
Third lithium chloride isoconcentrate [LiCl] = $3.75 \cdot 10^{-3}$ mole/liter								
1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-4}$	0.218	0.182	0.315	0.483	0.440	0.102
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.190	0.174	0.282	0.438	0.410	0.093
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.164	0.163	0.254	0.393	0.372	0.083
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.137	0.148	0.220	0.342	0.325	0.075
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.130	0.132	0.188	0.292	0.280	0.063
6	5.10^{-4}	$7.5 \cdot 10^{-4}$	0.084	0.107	0.147	0.232	0.225	0.048
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.064	0.083	0.113	0.177	0.174	0.035
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.043	0.059	0.075	0.123	0.120	0.025
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.020	0.039	0.037	0.058	0.058	0.011

optical density than the second, and the second less density than the first, due to the lower concentration of the cobalt-chloride complex ions. Hence, adding ClO_4^- ions to $Co(ClO_4)_2$ + LiCl in acetone does not change the composition of the complex cobalt-chloride ion and does not affect the nature of its absorption spectrum.

Lithium bromide isoconcentrates of the $Co(ClO_4)_2$ + LiBr + LiCl + acetone system. The lithium bromide preparations were gotten up as described by us previously [3]. The solution compositions and optical densities are listed in Table 2. As we see from the table, adding lithium bromide to $Co(ClO_4)_2$ + LiCl + acetone mixtures changes both the solutions's absorption spectra and the position of their maxima. As we know from the literature and from our own observations, the maximum absorption is shifted toward the longer wavelengths in the transition from complex cobalt-chloride ions to cobalt-bromide ones, [4].

TABLE 4

Isoconcentrates of Lithium Bromide: $Co(ClO_4)_2$ + LiCl + LiBr in Ethyl Alcohol: Overall Concentration: 0.005 mole/liter

Solution No.	Solution composition Concentration (mole/liter)		$\bar{D}$ at λ (in mμ)					
	$Co(ClO_4)_2$	LiCl	600	625	650	675	700	725
First lithium bromide isoconcentrate [LiBr] = $1.25 \cdot 10^{-3}$ mole/liter								
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-3}$	0.049	0.053	0.055	0.047	0.012	
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.091	0.104	0.110	0.091	0.024	
3	$2.625 \cdot 10^{-3}$	$1.125 \cdot 10^{-3}$	0.159	0.185	0.196	0.162	0.045	
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.244	0.294	0.326	0.268	0.081	
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.371	0.452	0.506	0.424	0.135	
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.496	0.606	0.688	0.587	0.192	
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.589	0.719	0.818	0.747	0.265	
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.547	0.672	0.799	0.746	0.282	
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.387	0.422	0.572	0.542	0.212	
Second lithium bromide isoconcentrate [LiBr] = $2.5 \cdot 10^{-3}$ mole/liter								
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	0.122	0.154	0.162	0.162	0.056	
2	2.10^{-3}	5.10^{-4}	0.165	0.213	0.230	0.222	0.079	
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$	0.221	0.285	0.311	0.294	0.106	
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.283	0.365	0.408	0.371	0.137	
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.345	0.446	0.504	0.455	0.172	
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.381	0.489	0.567	0.510	0.198	
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.390	0.496	0.589	0.537	0.217	
8	5.10^{-4}	2.10^{-3}	0.338	0.426	0.504	0.471	0.197	
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.221	0.276	0.332	0.315	0.132	
Third lithium bromide isoconcentrate [LiBr] = $3.75 \cdot 10^{-3}$ mole/liter								
1	$1.125 \cdot 10^{-3}$	$1.125 \cdot 10^{-4}$	0.177	0.242	0.260	0.280	0.120	0.022
2	1.10^{-3}	$2.5 \cdot 10^{-4}$	0.187	0.260	0.283	0.303	0.130	0.024
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.199	0.278	0.307	0.321	0.138	0.024
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.216	0.290	0.321	0.325	0.153	0.027
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.207	0.278	0.314	0.314	0.150	0.024
6	5.10^{-4}	$7.5 \cdot 10^{-4}$	0.196	0.260	0.294	0.296	0.143	0.022
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.173	0.232	0.265	0.262	0.125	0.021
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.135	0.178	0.207	0.202	0.092	0.017
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.078	0.103	0.120	0.118	0.056	0.008

In the first isoconcentrate the maxima are displaced toward a lower concentration of chlorine ions in the complex cobalt ion. The chlorine ions are displaced by the bromine ions in the complex ion. This displacement is not so great in the first isoconcentrate, however, as to change the nature of absorption in the complex chloride ions, the absorption maximum lying at λ = 675 mμ, which is typical of complex cobalt-chloride ions in acetone.

In the second isoconcentrate, the displacement of the chlorine ions by the bromine ions increases as the concentration of the lithium bromide is raised, causing a further shift of the maxima toward a lower concentration of chlorine ions in the complex cobalt ion and changing the nature of absorption in these complex ions. The complex ions exhibit an absorption maximum at λ = 700 mμ, which is evidence of a high percentage of bromine ions in the complex cobalt ion.

Further increase in the concentration of the lithium bromide (the third isoconcentrate) results in the disappearance of the maxima on the optical density –

composition curves for the $Co(ClO_4)_2$ + LiCl + LiBr + acetone system.

Instead of absorption curves with maxima, we get straight lines, which show that the absorption of complex cobalt ions drops as the cobalt-ion concentration is decreased. The chlorine ions were found to have no effect upon the absorption of solutions of the third isoconcentrate. This is borne out by the nature of the absorption, with a maximum at λ = 700 mμ, as well as by the disappearance of the maxima on the system's absorption curves.

Lithium chloride isoconcentrates of the $Co(ClO_4)_2$ + LiBr + LiCl + acetone system. We were also interested in tracing the influence of chlorine ions upon the location of the maxima on the absorption curves of the $Co(ClO_4)_2$ + LiBr + acetone system. The isoconcentrate solutions were prepared as specified above. The solution compositions and optical densities are listed in Table 3. As we see in this table, the phenomenon taking place is the same as that shown in Table 2, the difference being that here the chlorine ions displace the bromine ions in the complex cobalt ions, this being reflected in the absorption of the complex ions and in the location of the maxima. In the first isoconcentrate, the maximum absorption of the complex cobalt ions is found to lie at λ = 700 mμ, owing to the high bromine-ion concentration in the complex ions. As the percentage of lithium chloride is increased, the absorption maximum shifts toward the shorter wavelengths, indicating a substantial displacement of the bromine ions from the complex cobalt ions by the ions of chlorine (second isoconcentrate). The displacement of the bromine ions from the complex cobalt ions becomes complete as the concentration of the lithium chloride is raised still further (third isoconcentrate). In this case, the maxima on the optical density – composition curves for the $Co(ClO_4)_2$ + LiBr + LiCl + acetone system vanish, and absorption drops off as the cobalt-ion concentration is decreased. The bromine-ion concentration has no effect upon the absorption of complex cobalt ions, if we except the barely perceptible maximum at λ = 600 mμ.

Lithium bromide isoconcentrates in the $Co(ClO_4)_2$ + LiCl + LiBr + ethyl alcohol system. To test the influence of the solvent upon the location of the maxima on the optical density – composition curve as the system concentration is changed by adding halogen ions, we investigated the lithium bromide isoconcentrates of the $Co(ClO_4)_2$ + LiCl + LiBr + ethyl alcohol system. The preparation of the isoconcentrate solutions is seen in Table 4, which also lists the optical densities. Examination of the isoconcentrates indicates that the position of the maxima on the optical density – composition curve and the nature of absorption in complex cobalt ions both change as lithium bromide is added to the $Co(ClO_4)_2$ + LiCl + ethyl alcohol system, though the changes are less marked in the ethyl alcohol solutions than they are in acetone. As the concentration of lithium bromide is increased, the maximum absorption is shifted toward the longer wavelengths, owing to the bromine ions displacing the chlorine ions in the complex cobalt ions. The maximum on the optical density – composition curves for the $Co(ClO_4)_2$ + LiCl + LiBr + ethyl alcohol system is shifted toward a lower chlorine-ion concentration in the complex cobalt ion as the concentration of lithium bromide is raised. The extent of this shift increases as we pass from the first isoconcentrate to the third, though the maxima do not vanish, as was the case with the third lithium bromide isoconcentrate in the $Co(ClO_4)_2$ + LiCl + LiBr + acetone system.

This indicates that all the chlorine atoms are not displaced by bromine ions even in the third lithium bromide isoconcentrate concentrations, whereas in the third lithium bromide isoconcentrate of the $Co(ClO_4)_2$ + LiCl + LiBr + acetone system, all the chlorine ions were displaced by bromine ions in the complex cobalt ions.

Hence, the nature of the displacement of halogen ions from complex cobalt ions by other halogens depends upon the nature of the solvent as well as upon the ratio of the halogen-ion concentrations in the system.

TABLE 5

Isoconcentrates of Lithium Iodide: $Co(ClO_4)_2$ + LiCl + LiI in Ethyl Alcohol: Overall concentration 0.005 mole/liter

Solution No.	Solution composition Concentration (mole/liter)		$\bar{D}$ at λ (in mμ)				
	$Co(ClO_4)_2$	LiI	600	625	650	675	700
	First lithium iodide isoconcentrate [LiI] = $1.25 \cdot 10^{-3}$ mole/liter						
1	$3.375 \cdot 10^{-3}$	$3.75 \cdot 10^{-4}$	0.009	0.008	0.009	0.007	0.006
2	3.10^{-3}	$7.5 \cdot 10^{-4}$	0.025	0.029	0.030	0.023	0.007
3	$2.625 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.053	0.060	0.060	0.047	0.016
4	$2.25 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.098	0.116	0.124	0.098	0.029
5	$1.875 \cdot 10^{-3}$	$1.875 \cdot 10^{-3}$	0.164	0.193	0.213	0.164	0.052
6	$1.5 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.250	0.296	0.331	0.264	0.082
7	$1.125 \cdot 10^{-3}$	$2.625 \cdot 10^{-3}$	0.317	0.386	0.447	0.373	0.120
8	$7.5 \cdot 10^{-4}$	3.10^{-3}	0.322	0.394	0.463	0.407	0.138
9	$3.75 \cdot 10^{-4}$	$3.375 \cdot 10^{-3}$	0.232	0.285	0.340	0.310	0.108
	Second lithium iodide isoconcentrate [LiI] = $2.5 \cdot 10^{-3}$ mole/liter						
1	$2.25 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	0.014	0.015	0.017	0.013	0.009
2	2.10^{-3}	5.10^{-3}	0.025	0.030	0.031	0.027	0.013
3	$1.75 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	0.047	0.054	0.054	0.048	0.021
4	$1.5 \cdot 10^{-3}$	1.10^{-3}	0.073	0.091	0.098	0.076	0.031
5	$1.25 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.105	0.131	0.143	0.114	0.044
6	1.10^{-3}	$1.5 \cdot 10^{-3}$	0.140	0.174	0.194	0.156	0.058
7	$7.5 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	0.171	0.211	0.241	0.200	0.072
8	5.10^{-4}	2.10^{-3}	0.165	0.205	0.237	0.203	0.074
9	$2.5 \cdot 10^{-4}$	$2.25 \cdot 10^{-3}$	0.112	0.143	0.167	0.147	0.053
	Third lithium iodide isoconcentrate [LiI] = $3.75 \cdot 10^{-3}$ mole/liter						
1	$1.125 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	0.015	0.019	0.020	0.018	0.013
2	1.10^{-3}	$2.5 \cdot 10^{-3}$	0.022	0.027	0.028	0.025	0.016
3	$8.75 \cdot 10^{-4}$	$3.75 \cdot 10^{-4}$	0.028	0.034	0.037	0.032	0.018
4	$7.5 \cdot 10^{-4}$	5.10^{-4}	0.038	0.047	0.050	0.043	0.022
5	$6.25 \cdot 10^{-4}$	$6.25 \cdot 10^{-4}$	0.045	0.057	0.061	0.052	0.023
6	5.10^{-4}	$7.5 \cdot 10^{-4}$	0.047	0.062	0.067	0.056	0.024
7	$3.75 \cdot 10^{-4}$	$8.75 \cdot 10^{-4}$	0.050	0.065	0.071	0.058	0.025
8	$2.5 \cdot 10^{-4}$	1.10^{-3}	0.047	0.061	0.068	0.058	0.023
9	$1.25 \cdot 10^{-4}$	$1.125 \cdot 10^{-3}$	0.027	0.037	0.043	0.036	0.013

Lithium iodide isoconcentrates in the $Co(ClO_4)_2$ + LiCl + LiI + ethyl alcohol system. We also tried to find out how the iodine ion affects the position of the maxima in the $Co(ClO_4)_2$ + LiCl + ethyl alcohol system. Inasmuch as acetone solutions of cobalt iodide grow turbid very rapidly, owing to the appearance of a highly dispersed precipitate, we confined our observations to ethyl alcohol solutions.

The solution compositions and optical densities are given in Table 5.

Examination of Table 5 indicates that adding lithium iodide to the $Co(ClO_4)_2$ + LiCl + ethyl alcohol system shifts the maxima of the optical density – composition absorption curves, though the shift is much less than in the lithium bromide isoconcentrates of the $Co(ClO_4)_2$ + LiCl + ethyl alcohol system. When we compare the position of the maxima in the lithium bromide isoconcentrate (Table 4) with those for the lithium iodide (Table 5), we see that they are shifted to the left in the first case, i.e., toward a lower chlorine-ion concentration in the complex cobalt ion, whereas in the lithium iodide isoconcentrates the maxima are in the right-hand portion of the diagram, indicating only slight displacement of the chlorine ions in the complex cobalt ions by the iodine ions.

As we see in Table 5, the nature of absorption of cobalt complex ions of the lithium iodide isoconcentrate does not change as the concentration of lithium iodide is increased in the $Co(ClO_4)_2$ +LiCl + LiI + ethyl alcohol system. The maximum absorption occurs at λ = 650 mμ in complex cobalt ions of the lithium iodide isoconcentrate, this figure being typical of the absorption of complex cobalt-chloride ions in ethyl alcohol. If the chlorine ions were substantially displaced from the complex cobalt ions by iodine ions, the absorption maximum would be shifted toward the longer wavelengths, which did not take place.

Hence, comparison of the lithium bromide isoconcentrates of the $Co(ClO_4)_2$ + LiCl + LiBr + ethyl alcohol system with the lithium iodide isoconcentrates of the $Co(ClO_4)_2$ + LiCl + LiI + ethyl alcohol system (Tables 4 and 5) indicates that in alcoholic solutions the iodine ion is less able to displace chlorine ions from complex cobalt ions than is the bromine ion.

SUMMARY

1. The position of the maxima on the optical density – composition curves of the systems: $Co(ClO_4)_2$ + LiCl + LiBr + acetone and ethyl alcohol has been explored by varying the system concentration of ClO_4^-, Cl^-, Br^-, and I^- ions.

2. The addition of lithium perchlorate to the $Co(ClO_4)_2$ + LiCl + acetone system has no effect upon the position of the maxima on the optical density – composition curves or on the nature of the absorption spectra.

3. The addition of lithium bromide to the $Co(ClO_4)_2$ + LiCl + acetone system produces a shift of the maxima on the optical density – composition curves, the maxima disappearing as the concentration of lithium bromide is increased. The lithium bromide also changes the nature of absorption in complex cobalt – halid ions.

4. The position of the maxima on the optical density – composition curves in the $Co(ClO_4)_2$ + LiCl + ethyl alcohol system when lithium bromide and iodide are added has been explored. The addition of lithium bromide and iodide cause the maxima to shift but not to disappear altogether.

The bromine ion displaces the chlorine ion from a complex cobalt-chloride ion more readily than does the iodine ion.

LITERATURE CITED

[1] A.K.Babko, Proc. Inst. Chem., Ukrain. Acad. Sci., 8, 3 (1948); Job., Ann. chim., 9, 113 (1928).

[2] Potylitsyn, J. Russ. Phys.Chem.Soc., 20, 559 (1889).

[3] M.S.Barvinok, J.Gen.Chem. 19, 1028 (1949).*

[4] Brode and Morton, Proc. Royal Soc., 120 (A), 21 (1928); M.S.Barvinok, Bull. USSR Acad. Sci., Div. Phys., 12, 636 (1948).

Received July 24, 1949

* See C.B. Translation, p. 1019 ff.

SPECTROPHOTOMETRIC INVESTIGATION OF THE MAXIMA ON THE OPTICAL DENSITY - COMPOSITION CURVES OF SOLUTIONS OF COBALT HALIDES WHEN THE SYSTEM CONCENTRATION IS CHANGED

II. Cobalt (II) - Bromide Complexes in Ethyl Alcohol

M. S. Barvinok

Owing to remarkable properties of its alloys, cobalt has been widely utilized in industry and military engineering during the past few years, making the study of the physicochemical properties of cobalt compounds extremely important. The solutions of halides of divalent cobalt have attracted the attention of research workers for a long time, mainly because of their ability to change color, depending upon concentration, temperature, and the nature of the solvent. Some authors have attributed the change in the color of solutions of cobalt halide with the nature of the solvent when the halide ions are present in excess, when the temperature is raised, or when the concentration is increased, to an assumed ability of cobalt ions to form coordination compounds with halogen ions, the most likely composition of which is $CoCl_4^{--}$ [1]; others consider this phenomenon to be caused by dehydration of the cobalt ion [2].

We have found complex cobalt (II) - chloride ions present in solutions of cobalt halides when their color changed from pink to blue, using for this purpose the methods of physicochemical analysis, investigating the system's optical density [3]. The maximum absorption of these complex ions is located at various regions of the spectrum in different solvents, however. This indicates that the complex ions are solvated.

The change in the color of solutions of cobalt halides is accompanied by the formation of complex ions and by solvation.

The composition of the coordination compound formed in the solution from the constituents A and B in accordance with the equation $mA + nB = A_mB_n$ will be known as soon as we know m and n, A being the metallic ion, say, while B is any molecule or simple or complex anion. The method of continuous changes (in the composition - property diagram) that we employed [4] enables us to determine m/n. The system property we investigated was the optical density D, which was measured as the difference between the observed optical density of the components A + B in solution ($D_{obs.}$) and the sum of the total optical densities of the individual components, $D_1 + D_2$.

Hence, $D = D_{obs.} - (D_1 + D_2)$.

If the coordination compound A_mB_n possesses a characteristic color, the optical density versus composition curve will possess a maximum or a minimum.

We know from experiment that every coordination compound is stable in solution under certain physicochemical conditions. In most cases its dissociation is gradual, as these conditions approach the 'boundary' ones. Within the stable state region, the absicssa (the composition) of the point in the diagram

TABLE 1

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration = 0.1 m.

Solution No.	Solution composition		Concentration, mols/l		Optical density $D_{observed}$ at λ, mμ					$\bar{D}$ at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	$Co(ClO_4)_2$	LiBr	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.09	0.01	0.036	0.035	0.031	0.026	0.014	0.008	0.007	0.007	0.004	0.001
I	4.5	0	0.09	–	0.048	0.040	0.038	0.030	0.015					
2	4.0	1.0	0.08	0.02	0.050	0.051	0.050	0.045	0.021	0.007	0.016	0.016	0.018	0.001
II	4.0	0	0.08	–	0.043	0.035	0.034	0.027	0.020					
3	3.5	1.5	0.07	0.03	0.078	0.090	0.090	0.091	0.039	0.040	0.057	0.060	0.065	0.021
III	3.5	0	0.07	–	0.038	0.033	0.030	0.026	0,018					
4	3.0	2.0	0.06	0.04	0.111	0.145	0.152	0.161	0.068	0.080	0.118	0.126	0.142	0.175
IV	3.0	0	0.06	–	0.031	0.027	0.026	0.019	0.011					
5	2.5	2.5	0.05	0.05	0.163	0.222	0.237	0.259	0.119	0.237	0.197	0.214	0.242	0.107
V	2.5	0	0.05	–	0.026	0.025	0.023	0.017	0.012					
6	2.0	3.0	0.05	0.06	0.238	0.331	0.363	0.407	0.205	0.215	0.344	0.344	0.393	0.190
VI	2.0	0	0.05	–	0.023	0.020	0.019	0.014	0.015					
7	1.5	3.5	0.03	0.07	0.292	0.427	0.481	0.554	0.308	0.277	0.402	0.467	0.546	0.304
VII	1.5	0	0.03	–	0.015	0.015	0.014	0.008	0.004					
8	1.0	4.0	0.02	0.08	0.318	0.479	0.541	0.536	0.387	0.306	0.467	0.531	0.630	0.383
VIII	1.0	0	0.02	–	0.012	0.012	0.010	0.006	0.004					
9	0.5	4.5	0.01	0.09	0.257	0.398	0.456	0.545	0.362	0.251	0.390	0.450	0.541	0.362
IX	0.5	0	0.01	–	0.006	0.008	0.006	0.004	0					

representing the coordination compound A_mB_n does not change as the result of changes governing equilibrium, except for compounds of variable composition. The two sections of the curve that exhibits the given maximum or minimum meet at an angle that grows increasingly acute as the boundaries of the stable-state region are neared, thus making the maximum or minimum more distinct.

In our first report, we discussed the results of spectrophotometric measurements to determine the "boundary" conditions for the stability of cobalt (II) – chloride coordination compounds in ethyl alcohol. In the present report we set forth the results of our spectrophotometric investigation of solutions of cobalt (II) – bromide coordination compounds in ethyl alcohol at various system concentrations.

EXPERIMENTAL

We investigated the $Co(ClO_4)_2$ – LiBr – C_2H_5OH system. We used $Co(ClO_4)_2 \cdot 6H_2O$ as the cobalt preparation, since we had observed that the ClO_4^- ions had no effect upon the position of the point in the diagram representing the composition of the cobalt-halide coordination compound. We prepared the cobalt perchlorate from chemically pure cobalt carbonate, free of nickel, and chemically pure perchloric acid.

TABLE 2

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration 0.09 M.

Solution No.	Solution composition				Optical density, $D_{observed}$ at λ, mμ					$\bar{D}$ at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	Concentration, mol/liter $Co(ClO_4)_2$	LiBr	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.081	0.009	0.032	0.033	0.029	0.023	0.013	0	0.007	0.007	0.008	0.007
I	4.5	0	0.081	–	0.032	0.026	0.022	0.015	0.006					
2	4.0	1.0	0.072	0.018	0.045	0.047	0.052	0.042	0.019	0.014	0.022	0.031	0.027	0.012
II	4.0	0	0.072	–	0.031	0.025	0.021	0.014	0.007					
3	3.5	1.5	0.063	0.027	0.071	0.084	0.082	0.084	0.035	0.043	0.062	0.064	0.070	0.028
III	3.5	0	0.063	–	0.028	0.022	0.018	0.014	0.007					
4	3.0	2.0	0.054	0.036	0.108	0.131	0.138	0.137	0.052	0.085	0.115	0.123	0.130	0.049
IV	3.0	0	0.054	–	0.023	0.016	0.115	0.007	0.003					
5	2.5	2.5	0.045	0.045	0.163	0.222	0.232	0.243	0.101	0.143	0.207	0.219	0.235	0.096
V	2.5	0	0.045	–	0.020	0.015	0.013	0.008	0.005					
6	2.0	3.0	0.036	0.054	0.215	0.329	0.344	0.361	0.160	0.199	0.318	0.333	0.357	0.156
VI	2.0	0	0.036	–	0.016	0.011	0.011	0.004	0.004					
7	1.5	3.5	0.027	0.063	0.265	0.389	0.432	0.465	0.236	0.253	0.381	0.424	0.457	0.236
VII	1.5	0	0.027	–	0.012	0.008	0.008	0.008	0					
8	1.0	4.0	0.018	0.072	0.292	0.439	0.491	0.538	0.308	0.283	0.433	0.484	0.531	0.308
VIII	1.0	0	0.018	–	0.009	0.006	0.007	0.007	0					
9	0.5	4.5	0.009	0.081	0.231	0.361	0.401	0.457	0.280	0.228	0.259	0.399	0.454	0.280
IX	0.5	0	0.009	–	0.003	0.002	0.002	0.003	0					

TABLE 3 Overall Concentration 0.08 M

1	4.5	0.5	0.072	0.008	0.040	0.032	0.030	0.023	0.013	0.009	0.009	0.008	0.008	0.003
I	4.5	0	0.072	–	0.031	0.023	0.022	0.015	0.010					
2	4.0	1.0	0.064	0.016	0.047	0.041	0.038	0.033	0.015	0.019	0.019	0.017	0.019	0.005
II	4.0	0	0.064	–	0.028	0.022	0.021	0.014	0.010					
3	3.5	1.5	0.056	0.024	0.062	0.058	0.056	0.052	0.021	0.037	0.038	0.038	0.039	0.013
III	3.5	0	0.056	–	0.025	0.020	0.018	0.013	0.008					
4	3.0	2.0	0.048	0.032	0.088	0.095	0.091	0.088	0.035	0.067	0.079	0.077	0.078	0.031
IV	3.0	0	0.048	–	0.021	0.016	0.014	0.010	0.004					
5	2.5	2.5	0.040	0.040	0.125	0.143	0.142	0.141	0.058	0.107	0.129	0.134	0.132	0.054
V	2.5	0	0.040	–	0.018	0.014	0.008	0.009	0.004					
6	2.0	3.0	0.032	0.048	0.166	0.205	0.205	0.211	0.095	0.152	0.194	0.196	0.202	0.095
VI	2.0	0	0.032	–	0.014	0.011	0.009	0.009	0					
7	1.5	3.5	0.024	0.056	0.213	0.280	0.298	0.318	0.150	0.203	0.273	0.291	0.317	0.150
VII	1.5	0	0.024	–	0.010	0.007	0.007	0.001	0					
8	1.0	4.0	0.016	0.064	0.225	0.310	0.326	0.360	0.190	0.219	0.306	0.318	0.359	0.190
VIII	1.0	0	0.016	–	0.006	0.004	0.008	0.001	0					
9	0.5	4.5	0.008	0.072	0.178	0.258	0.270	0.304	0.173	0.175	0.256	0.268	0.303	0.173
IX	0.5	0	0.008	–	0.003	0.002	0.002	0.001	0					

TABLE 4

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration 0.07 M

Solution No.	Solution composition				Optical density $D_{obs.}$ at λ, mμ					δ at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	Concentration, mol-liter		600	625	650	675	700	600	625	650	675	700
			$Co(ClO_4)_2$	LiBr										
1	4.5	0.5	0.063	0.007	0.036	0.031	0.027	0.018	0.015	0.009	0.009	0.007	0.007	0.008
I	4.5	0	0.063	–	0.027	0.022	0.020	0.011	0.007					
2	4.0	1.0	0.056	0.014	0.042	0.038	0.033	0.024	0.016	0.009	0.018	0.014	0.013	0.009
II	4.0	0	0.056	–	0.023	0.020	0.019	0.011	0.007					
3	3.5	1.5	0.049	0.021	0.055	0.053	0.051	0.041	0.018	0.036	0.036	0.035	0.031	0.012
III	3.5	0	0.049	–	0.020	0.017	0.016	0.010	0.006					
4	3.0	2.0	0.042	0.028	0.086	0.088	0.087	0.081	0.031	0.070	0.076	0.076	0.074	0.020
IV	3.0	0	0.042	–	0.016	0.012	0.011	0.007	0.011					
5	2.5	2.5	0.035	0.035	0.016	0.132	0.132	0.130	0.048	0.102	0.121	0.122	0.123	0.046
V	2.5	0	0.035	–	0.014	0.011	0.010	0.007	0.002					
6	2.0	3.0	0.028	0.042	0.147	0.182	0.182	0.186	0.073	0.134	0.172	0.173	0.179	0.070
VI	2.0	0	0.028	–	0.013	0.010	0.009	0.007	0.003					
7	1.5	3.5	0.021	0.049	0.185	0.238	0.246	0.260	0.118	0.177	0.231	0.243	0.258	0.018
VII	1.5	0	0.021	–	0.008	0.007	0.003	0.002	0.118					
8	1.0	4.0	0.014	0.056	0.195	0.260	0.275	0.295	0.144	0.188	0.255	0.273	0.293	0.144
VIII	1.0	0	0.014	–	0.007	0.005	0.002	0.002	0					
9	0.5	4.5	0.007	0.063	0.144	0.200	0.212	0.235	0.126	0.141	0.197	0.210	0.233	0.126
IX	0.5	0	0.007	–	0.003	0.003	0.002	0.002	0					

TABLE 5 Overall Concentration 0.06 M

1	4.5	0.5	0.054	0.006	0.030	0.024	0.023	0.015	0.013	0.009	0.009	0.008	0.004	0.009
I	4.5	0	0.054	–	0.021	0.015	0.015	0.011	0.004					
2	4.0	1.0	0.048	0.012	0.039	0.033	0.032	0.025	0.015	0.020	0.018	0.019	0.014	0.009
II	4.0	0	0.048	–	0.019	0.015	0.015	0.011	0.006					
3	3.5	1.5	0.042	0.018	0.045	0.041	0.040	0.033	0.015	0.028	0.029	0.029	0.024	0.011
III	3.5	0	0.042	–	0.017	0.012	0.011	0.009	0.004					
4	3.0	2.0	0.036	0.024	0.064	0.070	0.066	0.064	0.025	0.050	0.060	0.058	0.058	0.022
IV	3.0	0	0.036	–	0.014	0.010	0.008	0.006	0.003					
5	2.5	2.5	0.030	0.030	0.094	0.108	0.104	0.102	0.039	0.081	0.098	0.096	0.096	0.036
V	2.5	0	0.030	–	0.013	0.010	0.008	0.006	0.003					
6	2.0	3.0	0.024	0.036	0.114	0.141	0.140	0.141	0.054	0.105	0.133	0.134	0.136	0.051
VI	2.0	0	0.024	–	0.009	0.008	0.006	0.005	0.003					
7	1.5	3.5	0.018	0.042	0.145	0.185	0.188	0.195	0.084	0.139	0.181	0.185	0.193	0.084
VII	1.5	0	0.018	–	0.006	0.004	0.003	0.002	0					
8	1.0	4.0	0.012	0.048	0.151	0.196	0.201	0.213	0.100	0.145	0.192	0.198	0.211	0.100
VIII	1.0	0	0.012	–	0.006	0.004	0.003	0.002	0					
9	0.5	4.5	0.006	0.054	0.113	0.150	0.154	0.172	0.082	0.111	0.150	0.152	0.172	0.082
IX	0.5	0	0.006	–	0.002	0	0	0	0					

TABLE 6

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration 0.05 M

Solution No.	Solution composition				Optical density D_{obs} at λ, mμ					β at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	Concentration, mol/liter $Co(ClO_4)_2$	LiBr	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.045	0.005	0.023	0.020	0.018	0.014	0.008	0.005	0.005	0.006	0.004	0.001
I	4.5	0	0.045	0	0.018	0.015	0.012	0.010	0.007					
2	4.0	1.0	0.040	0.010	0.028	0.025	0.023	0.020	0.008	0.009	0.010	0.010	0.010	0.001
II	4.0	0	0.040	0	0.019	0.015	0.013	0.010	0.007					
3	3.5	1.5	0.035	0.015	0.037	0.037	0.036	0.033	0.011	0.024	0.024	0.023	0.026	0.008
III	3.5	0	0.035	0	0.013	0.013	0.003	0.007	0.003					
4	3.0	2.0	0.030	0.020	0.056	0.062	0.062	0.060	0.021	0.043	0.052	0.054	0.053	0.019
IV	3.0	0	0.030	0	0.013	0.010	0.008	0.007	0.002					
5	2.5	2.5	0.030	0.025	0.076	0.090	0.092	0.092	0.032	0.067	0.082	0.085	0.087	0.032
V	2.5	0	0.025	0	0.009	0.008	0.007	0.005	0					
6	2.0	3.0	0.020	0.030	0.108	0.132	0.135	0.138	0.052	0.101	0.126	0.132	0.134	0.052
VI	2.0	0	0.020	0	0.007	0.006	0.003	0.004	0					
7	1.5	3.5	0.015	0.035	0.130	0.170	0.178	0.183	0.075	0.125	0.171	0.175	0.181	0.074
VII	1.5	0	0.015	0	0.005	0.003	0.003	0.002	0.001					
8	1.0	4.0	0.010	0.040	0.128	0.178	0.185	0.193	0.085	0.123	0.175	0.182	0.191	0.084
VIII	1.0	0	0.010	0	0.005	0.003	0.003	0.002	0.001					
9	0.5	4.5	0.005	0.045	0.090	0.131	0.138	0.144	0.068	0.088	0.131	0.138	0.144	0.067
IX	0.5	0	0.005	0	0.002	0	0	0	0					

TABLE 7 Overall Concentration 0.04 M

1	4.5	0.5	0.036	0.004	0.016	0.012	0.011	0.008	0.006	0	0	0	0	0.002
I	4.5	0	0.036	–	0.016	0.012	0.011	0.008	0.004					
2	4.0	1.0	0.032	0.008	0.021	0.016	0.016	0.014	0.006	0.003	0.001	0.003	0.003	0
II	4.0	0	0.032	–	0.019	0.015	0.013	0.011	0.006					
3	3.5	1.5	0.038	0.012	0.028	0.025	0.026	0.025	0.008	0.011	0.013	0.015	0.016	0.003
III	3.5	0	0.038	–	0.017	0.012	0.011	0.009	0.005					
4	3.0	2.0	0.024	0.016	0.043	0.045	0.045	0.045	0.015	0.029	0.035	0.037	0.039	0.012
IV	3.0	0	0.024	–	0,014	0.010	0.008	0.006	0.003					
5	2.5	2.5	0.020	0.020	0.062	0.072	0.072	0.075	0.023	0.049	0.062	0.064	0.069	0.020
V	2.5	0	0.020	–	0.013	0.010	0.008	0.006	0.003					
6	2.0	3.0	0.016	0.024	0.075	0.095	0.100	0.105	0.033	0.066	0.087	0.094	0.100	0.030
VI	2.0	0	0.016	–	0.009	0.008	0.006	0.005	0.003					
7	1.5	3.5	0.012	0.028	0.096	0.123	0.128	0.138	0.048	0.090	0.119	0.125	0.138	0.048
VII	1.5	0	0.012	–	0.006	0.004	0.003	0	0					
8	1.0	4.0	0.008	0.032	0.095	0.127	0.135	0.147	0.056	0.089	0.123	0.132	0.147	0.056
VIII	1.0	0	0.008	–	0.006	0.004	0.003	0	0					
9	0.5	4.5	0.004	0.036	0.065	0.096	0.097	0.108	0.044	0.063	0.096	0.095	0.108	0.044
IX	0.5	0	0.004	–	0.002	0	0.002	0	0					

TABLE 8

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration 0.03 M

Solution No.	Solution composition				Optical density, $D_{obs.}$ at λ, mμ					D at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	Concentration, mol/liter $Co(ClO_4)_2$	LiBr	600	625	650	67.	700	600	625	650	675	700
1	4.5	0.5	0.027	0.003	0.018	0.013	0.011	0.008	0.006	0.005	0.003	0.008	0.008	0.006
I	4.5	0	0.027	–	0.013	0.010	0.003	0	0					
2	4.0	1.0	0.024	0.006	0.020	0.015	0.013	0.011	0.005	0.007	0.005	0.010	0.011	0.005
II	4.0	0	0.024	–	0.013	0.010	0.003	0	0					
3	3.5	1.5	0.021	0.009	0.028	0.025	0.022	0.020	0.005	0.020	0.017	0.020	0.020	0.005
III	3.5	0	0.021	–	0.008	0.008	0.002	0	0					
4	3.0	2.0	0.018	0.012	0.041	0.046	0.043	0.040	0.015	0.028	0.043	0.038	0.040	0.015
IV	3.0	0	0.018	–	0.013	0.003	0.005	0	0					
5	2.5	2.5	0.015	0.015	0.056	0.064	0.065	0.063	0.023	0.043	0.061	0.063	0.063	0.023
V	2.5	0	0.015	–	0.013	0.003	0.002	0	0					
6	2.0	3.0	0.012	0.018	0.070	0.085	0.090	0.089	0.028	0.064	0.083	0.090	0.089	0.028
VI	2.0	0	0.012	–	0.007	0.002	0	0	0					
7	1.5	3.5	0.009	0.021	0.082	0.111	0.115	0.120	0.043	0.079	0.111	0.115	0.120	0.043
VII	1.5	0	0.009	–	0.003	0	0	0	0					
8	1.0	4.0	0.006	0.024	0.080	0.112	0.118	0.125	0.048	0.077	0.112	0.018	0.125	0.048
VIII	1.0	0	0.006	–	0.003	0	0	0	0					
9	0.5	4.5	0.003	0.027	0.060	0.080	0.085	0.090	0.036	0.059	0.080	0.085	0.090	0.036
IX	0.5	0	0.003	–	0.001	0	0	0	0					

TABLE 9 Overall Concentration 0.02 M

1	4.5	0.5	0.018	0.002	0.008	0.007	0.005	0.003	0.002	0.000	0.002	0.003	0.003	0.002
I	4.5	0	0.018	–	0.008	0.005	0.002	0	0					
2	4.0	1.0	0.016	0.004	0.013	0.010	0.008	0.007	0.002	0.004	0.005	0.006	0.007	0.002
II	4.0	0	0.016	–	0.009	0 005	0.002	0	0					
3	3.5	1.5	0.014	0.006	0.017	0.014	0.013	0.011	0.002	0.008	0.009	0.011	0.011	0.002
III	3.5	0	0.014	–	0.009	0.005	0.002	0	0					
4	3.0	2.0	0.012	0.008	0.025	0.023	0.023	0.023	0.007	0.017	0.019	0.023	0.023	0.007
IV	3.0	0	0.012	–	0.008	0.004	0	0	0					
5	2.5	2.5	0.010	0.010	0.030	0.034	0.034	0.034	0.009	0.023	0.031	0.034	0.034	0.009
V	2.5	0	0.010	–	0.007	0.003	0	0	0					
6	2.0	3.0	0.008	0.012	0.038	0.043	0.043	0.044	0.010	0.033	0.041	0.043	0.044	0.010
VI	2.0	0	0.008	–	0.005	0.002	0	0	0					
7	1.5	3.5	0.006	0.014	0.045	0.057	0.058	0.060	0.017	0.042	0.057	0.058	0.060	0.017
VII	1.5	0	0.006	–	0.003	0	0	0	0					
8	1.0	4.0	0.004	0.016	0.043	0.057	0.058	0.061	0.024	0.040	0.057	0.058	0.061	0.024
VIII	1.0	0	0.004	–	0.003	0	0	0	0					
9	0.5	4.5	0.002	0.018	0.028	0.040	0.045	0.044	0.010	0.025	0.040	0.045	0.044	0.010
IX	0.5	0	0.002	–	0.003	0	0	0	0					

TABLE 10

Optical Density of Alcoholic Solutions of Cobalt Perchlorate in the Presence of Lithium Bromide – Overall Concentration 0.01 M

Solution No.	Composition of solution				Optical density $D_{obs.}$ at λ, mμ					$\bar{D}$ at λ, mμ				
	$Co(ClO_4)_2$, ml	LiBr, ml	Composition, mol/liter $Co(ClO_4)_2$	LiBr	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.009	0.001	0.007	0.003	0.008	0.002		0.007	0.003	0.008	0.002	
I	4.5	0	0.009	–	0	0	0	0						
2	4.0	1.0	0.008	0.002	0.005	0.002	0.005	0		0.005	0.002	0.005	0	
II	4.0	0	0.008	–	0	0	0	0						
3	3.5	1.5	0.007	0.003	0.005	0.001	0.005	0		0.005	0.001	0.005	0	
III	3.5	0	0.007	–	0	0	0	0						
4	3.0	2.0	0.006	0.004	0.010	0.008	0.008	0.007		0.010	0.008	0.008	0.007	
IV	3.0	0	0.006	–	0	0	0	0						
5	2.5	2.5	0.005	0.005	0.014	0.013	0.013	0.012		0.014	0.013	0.013	0.012	
V	2.5	0	0.005	–	0	0	0	0						
6	2.0	3.0	0.004	0.006	0.013	0.012	0.012	0.011		0.013	0.012	0.012	0.011	
VI	2.0	0	0.004	–	0	0	0	0						
7	1.5	3.5	0.003	0.007	0.018	0.021	0.021	0.023		0.018	0.021	0.021	0.023	
VII	1.5	0	0.003	–	0	0	0	0						
8	1.0	4.0	0.002	0.008	0.017	0.020	0.019	0.023		0.017	0.020	0.019	0.023	
VIII	1.0	0	0.002	–	0	0	0	0						
9	0.5	4.5	0.001	0.009	0.010	0.012	0.010	0.018		0.010	0.012	0.010	0.018	
IX	0.5	0	0.001	–	0	0	0	0						

Before preparing the solutions, we recrystallized the $Co(ClO_4)_2 \cdot 6H_2O$ twice. The lithium bromide was prepared from chemically pure lithium carbonate and chemically pure hydrobromic acid. The solutions of lithium bromide in ethyl chloride were prepared from doubly recrystallized lithium bromide, which was first desiccated in an exsiccator and then dehydrated by heating to above 160° in a current of nitrogen. The ethyl alcohol was dehydrated as described in the literature [3] before the solutions were prepared.

The optical density was measured with a Beckmann quartz photoelectric spectrophotometer at a temperature of 20° ± 1°.

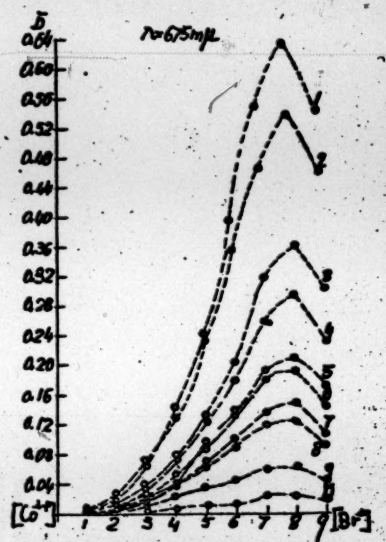
We explored ten different sections of the $Co(ClO_4)_2$ – LiBr – C_2H_5OH along a diagonal plane, with the following overall concentrations: 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, and 0.01 mole/liter. The solutions of each series were prepared by the method of continuous changes. They constituted mixtures of solutions of cobalt perchlorate and lithium bromide of the same polar concentration, the volume being kept constant at 5 ml and the molar concentration being kept constant at a value equal to the molar concentration of the cobalt perchlorate and lithium bromide solutions. The technique of preparing the solution in each series is evident from Tables 1-10.

The composition of the solutions and their optical densities are listed in Tables 1-10. The figure shows the graph of $\bar{D}$ versus composition for the various

solutions series at $\lambda = 675$ mμ

We see from the figure that the optical density of the solution decreases as we pass from the section with an overall concentration of 0.1 mole/liter to the section with overall concentration of 0.01 mole/liter, owing to the decreasing concentration of the complex ions. The maxima on the curves of optical density D versus composition lie at $m/n = 1:4$, where m is the number of cobalt ions in the complex ions, and n is the number of bromine ions in the complex ion. We had previously established that when the ratio of cobalt and bromine ions is the foregoing one in an ethyl-alcohol solution, the cobalt-bromide complex ions have the composition of $CoBr_4^{--}$.

The point in the diagram that represents the composition of the complex ion $CoBr_4^{--}$ does not shift along the composition axis until the total concentration in the $Co(ClO_4)_2$ – LiBr system in ethyl alcohol is 0.03 mole/liter.



Cobalt perchlorate + lithium bromide + ethyl alcohol.

Sections parallel to the cobalt perchlorate – lithium bromide side of the diagram.

The solution compositions for the curves 1-10 are given in the respective tables.

At a total concentration of 0.03 mole/liter and at $\lambda = 600$ mμ, we see that the maximum is shifted toward a lower percentage of bromine ions in the complex ion. This shift in the maximum is repeated at the overall concentration of 0.02 mole/liter in the $Co(ClO_4)_2$ – LiBr – ethyl alcohol system, at $\lambda = 600$, 625, 650, and 675 mμ. At a total concentration of 0.01 mole/liter in the $Co(ClO_4)_2$ – LiBr – ethyl alcohol system, the optical density at $\lambda = 700$ mμ has a value that lies within the limits of experimental error.

At $\lambda = 600$, 625, 650, and 675 mμ we see the displacement of the maximum toward a lower percentage of bromine ions in the complex ion repeated. Hence, in cobalt (II) – bromide complexes, the stable-state region approaches the "boundary" conditions at an overall concentration of 0.03 mole/liter in the $Co(ClO_4)_2$ – LiBr + acetone system. Beginning with this concentration, the abscissa (composition) of the point representing the complex ion $CoBr_4^{--}$ is displaced at an overall concentration of 0.01 mole/liter in cobalt (II)–chloride coordination compounds in ethyl alcohol. This bears out our earlier observation that the stability of cobalt (II) – chloride coordination compounds in ethyl alcohol is greater than that of cobalt (II) – bromide coordination compounds.

SUMMARY

1. A study has been made of the system $Co(ClO_4)_2$ – LiBr in ethyl alcohol at $\lambda = 600$, 625, 650, 675, and 700 mμ at overall concentrations of 0,1 to 0.01 mole/liter.

2. The stable-state region approaches the "boundary" conditions, where the abscissa (composition) of the point representing the complex ion $CoBr_4^{--}$ is displaced, at an overall concentration of 0.03 mole/liter.

3. Comparison of the "boundary" concentration for cobalt-bromide and cobalt chloride complex ions in ethyl alcohol is higher for the chlorides than for the bromides.

LITERATURE CITED

[1] Donnan and Basset, J. Chem. Soc., 81, 939 (1902).

[2] Jones and Uhler, Am. Chem. J., 37, 126 (1907); Robinson and Brown, Trans. Proc. Roy, Soc. New Zealand, 77, 1 (1948).

[3] Barvinok, Bull. USSR Acad. Sci., Div. Phys., 12, 636 (1948).

[4]Babko, Proc. Inst. Chem., Ukrain. Acad. Sci. 8, 3 (1946); Job., Ann. Chim., 8, 113 (1928).

[5] Palauzov. Chemical Reagents. United Scientific and Technical Press.

Received July 27, 1949.

THE VISCOSITY OF THE BINARY SYSTEMS: ALCOHOLS – DICHLOROETHANE

V. V. Udovenko, R. P. Airapetova, and R. I. Pilatova

The present paper discusses the viscosity of binary systems constituted by aliphatic alcohols and dichloroethane, the vapor pressure of which had been previously investigated in our laboratory [1].

In this research we used the following thoroughly purified substances: dichloroethane – b.p. 82.0° (728 mm); methanol – b.p. 63.5° (730 mm); ethyl alcohol – b.p. 77.5° (736 mm); propyl alcohol – b.p. 96.0° (729 mm); butyl alcohol – b.p. 115.5° (722 mm); and isoamyl alcohol – b.p. 129.0° (730 mm).

We explored the viscosity and density of the following systems: methanol – dichloroethane, ethyl alcohol – dichloroethane, propyl alcohol – dichloroethane, butyl alcohol – dichloroethane, and isoamyl alcohol – dichloroethane at 30, 40, 50, and 60°.

The results of our measurements of the viscosity and density of these systems are given in Tables 1, 2, 3, 4, and 5.

TABLE 1

Methanol – Dichloroethane

Molar % alcohol	Viscosity				Density			
	30°	40°	50°	60°	30°	40°	50°	60°
100.00	0.5229	0.4539	0.4023	0.3520	0.7861	0.7759	0.7681	0.7588
91.20	0.5488	0.4762	0.4199	0.3682	0.8594	0.8478	0.8388	0.8277
83.93	0.5617	0.4852	0.4255	0.3754	0.9107	0.8997	0.8887	0.8769
79.82	0.5696	0.4915	0.4323	0.3766	0.9375	0.9265	0.9147	0.9035
69.06	0.5824	0.5005	0.4422	0.3870	0.9978	0.9860	0.9738	0.9632
62.21	0.5936	0.5094	0.4506	0.3953	1.0354	1.0204	1.0082	0.9961
53.74	0.6032	0.5227	0.4587	0.4018	1.0718	1.0584	1.0450	1.0354
42.17	0.6125	0.5318	0.4709	0.4177	1.1175	1.1030	1.0913	1.0774
23.69	0.6407	0.5596	0.4990	0.4442	1.1788	1.1646	1.1520	1.1383
15.68	0.6585	0.5772	0.5169	0.4630	1.2023	1.1868	1.1740	1.1594
0.00	0.7256	0.6383	0.5724	0.5116	1.2405	1.2264	1.2124	1.1974

The viscosity isotherms of the methanol – dichloroethane system are S-shaped. Such a shape of the viscosity isotherms is evidence of interaction between the constituents [2].

In this system, however, the interaction of the constituents is accompanied by decomposition of the associated molecules of methanol, as had been observed earlier in the curves of vapor pressure [1].

TABLE 2

Ethyl Alcohol – Dichloroethane

Molar % alcohol	Viscosity				Density			
	30°	40°	50°	60°	30°	40°	50°	60°
100.00	0.9842	0.8165	0.6921	0.5839	0.7829	0.7735	0.7655	0.7564
88.19	0.8746	0.7374	0.6280	0.5335	0.8522	0.8450	0.8342	0.8257
75.20	0.7907	0.6671	0.5723	0.4917	0.9229	0.9121	0.9006	0.8902
59.89	0.7251	0.6178	0.5360	0.4651	0.9996	0.9877	0.9752	0.9636
47.26	0.6873	0.5895	0.5161	0.4500	1.0568	1.0440	1.0318	1.0176
39.12	0.6702	0.5806	0.5107	0.4478	1.0917	1.0775	1.0647	1.0520
32.79	0.6668	0.5767	0.5115	0.4493	1.1168	1.1027	1.0922	1.0780
22.95	0.6654	0.5787	0.5120	0.4552	1.1565	1.1420	1.1285	1.1143
12.15	0.6779	0.5938	0.5336	0.4753	1.1965	1.1826	1.1685	1.1529
6.40	0.6954	0.6126	0.5529	0.4954	1.2175	1.2021	1.1890	1.1733
0.00	0.7256	0.6383	0.5724	0.5116	1.2405	1.2264	1.2124	1.1974

TABLE 3

n-Propyl Alcohol – Dichloroethane

Molar % alcohol	Viscosity				Density			
	30°	40°	50°	60°	30°	40°	50°	60°
100.00	1.7680	1.3858	1.1280	0.9154	0.7964	0.7892	0.7818	0.7727
83.60	1.3280	1.0711	0.8872	0.7360	0.8724	0.8619	0.8533	0.8436
67.21	1.0340	0.8514	0.7210	0.6115	0.9462	0.9351	0.9243	0.9123
55.79	0.9007	0.7563	0.6484	0.5555	0.9965	0.9842	0.9734	0.9615
32.60	0.7263	0.6293	0.5542	0.4878	1.1147	1.1008	1.0879	1.0746
21.63	0.6888	0.6167	0.5488	0.4833	1.1455	1.1315	1.1168	1.1033
11.82	0.6969	0.6089	0.5483	0.4864	1.1887	1.1736	1.1604	1.1462
0.00	0.7256	0.6383	0.5724	0.5116	1.2405	1.2264	1.2124	1.1974

TABLE 4

n-Butyl Alcohol – Dichloroethane

Molar % alcohol	Viscosity				Density			
	30°	40°	50°	60°	30°	40°	50°	60°
100.00	2.2548	1.7589	1.4051	1.1267	0.8029	0.7958	0.7881	0.7803
85.60	1.7441	1.3785	1.1228	0.9313	0.8582	0.8495	0.8415	0.8340
67.68	1.2716	1.0360	0.8711	0.7288	0.9288	0.9184	0.9104	0.8925
56.18	1.0617	0.8734	0.7447	0.6357	0.9760	0.9650	0.9541	0.9438
46.83	0.9418	0.7892	0.6791	0.5838	1.0160	1.0052	0.9914	0.9815
31.78	0.8081	0.6920	0.6061	0.5310	1.0829	1.0706	1.0575	1.0459
20.52	0.7449	0.6427	0.5710	0.5040	1.1345	1.1201	1.1063	1.0942
9.69	0.7121	0.6205	0.5584	0.4978	1.1908	1.1752	1.1620	1.1482
0.00	0.7256	0.6383	0.5724	0.5116	1.2405	1.2264	1.2124	1.1974

The viscosity isotherms of the ethyl alcohol – dichloroethane, propyl alcohol – dichloroethane, and butyl alcohol – dichloroethane systems all traverse a minimum that is most prominent in the ethyl alcohol – dichloroethane system. In the propyl alcohol – dichloroethane system the viscosity minimum is less pronounced than in the preceding system, while it is even less distinct in the butyl alcohol – dichloroethane system. A similar state of affairs prevails in

TABLE 5

Isoamyl Alcohol – Dichloroethane

Molar % alcohol	Viscosity				Density			
	30°	40°	50°	60°	30°	40°	50°	60°
100.00	3.2671	2.4292	1.8674	1.4516	0.8040	0.7960	0.7685	0.7838
88.80	2.5105	1.9098	1.5072	1.1976	0.8397	0.8309	0.8229	0.8144
80.49	2.0808	1.6191	1.3091	1.0590	0.8674	0.8585	0.8503	0.8426
66.39	1.5321	1.2298	1.0146	0.8522	0.9180	0.9089	0.8983	0.8916
57.65	1.3016	1.0647	0.8917	0.7481	0.9519	0.9419	0.9315	0.9203
43.02	1.0286	0.8579	0.7365	0.6333	1.0127	1.0018	0.9910	0.9789
32.64	0.9054	0.7649	0.6650	0.5866	1.0612	1.0483	1.0369	1.0242
22.01	0.7970	0.6865	0.6030	0.5317	1.1123	1.1005	1.0871	1.0764
12.72	0.7430	0.6478	0.5786	0.5142	1.1635	1.1515	1.1366	1.1256
0.00	0.7256	0.6383	0.5724	0.5116	1.2405	1.2264	1.2124	1.1974

the vapor pressure diagrams, the maximum being most prominent in the methanol – dichloroethane system and least pronounced in the butyl alcohol – dichloroethane system. As we know, the minima on the viscosity isotherms and the maxima on the vapor-pressure curves are due to decomposition of the associated alcohol molecules when they are dissolved in dichloroethane.

Temperature affects the shape of the viscosity isotherms greatly, the effect of temperature on the shape of the viscosity isotherms being clearly evident from an inspection of the respective diagrams. As the temperature rises, the minima on the viscosity isotherms of the ethyl alcohol – dichloroethane, propyl alcohol – dichloroethane, and butyl alcohol – dichloroethane systems grow flatter and are displaced appreciably toward the alcohol.

Not enough light has been shed on the problem of the displacement of the minima on the viscosity isotherms with rising temperature in the literature on physicochemical analysis, V.Ya. Anosov and S.A.Pogodin [3], for example, believe that as the temperature rises, the viscosity minimum ought to shift toward the low viscosity component, citing as an example of this the acetone – carbon disulfide system investigated by O. Faust [4]. N.N.Efremov, on the other hand, made a study of the nitrobenzene – isobutyl alcohol system and found that "the position of the viscosity minimum does not remain constant, but is shifted toward the isobutyl alcohol, the high-viscosity constituent of the system, as the temperature is raised" [5].

We know of a few systems in the literature, with minima on the viscosity isotherms, that have been explored over a wide range of temperatures and can be utilized to decide the question of the direction of the shift of the minimum on the viscosity isotherms as the temperature is raised. These systems indicate that we do not possess enough experimental data at the present time to assert that the minima on viscosity isotherms are shifted toward the low-viscosity component as the temperature is raised. However, the data in the literature and our own experimental findings enable us to judge the direction in which the minimum on a viscosity isotherm should shift as the temperature is raised. Considering the systems we have explored, as well as the nitrobenzene – isobutyl alcohol system investigated by N.N.Efremov and the acetone – carbon disulfide system investigated by O. Faust, we conclude that in all these systems raising the temperature shifts the minimum toward the more highly associated component, which usually has the higher temperature coefficient of viscosity. Comparison of the temperature coefficients of viscosity of the components of the systems known to us that possess a viscosity minimum fully bears out the

correctness of this conclusion.

The viscosity isotherms of the isoamyl alcohol – dichloroethane system are convex toward the composition axis. The viscosity isotherms of this system have no minimum, just as its vapor pressure curves have no maximum [1]. The absence of a minimum on the viscosity isotherms and of a maximum on the vapor pressure curves is evidence that isoamyl alcohol is less associated than the other alcohols.

We also calculated the viscosities of the systems we investigated from the G.M.Panchenkov formula [6], and found that the calculated viscosities were in good agreement with the experimental values, for the pure substances as well as for the mixtures. The mean deviation of the experimental viscosity values from the computed ones does not exceed one per cent, with the exception of a few instances where it exceeds two per cent.

SUMMARY

1. A study has been made of the viscosity and density of five binary systems formed by dichloroethane with the following alcohols: methyl, ethyl, propyl, butyl, and isoamyl, at 30, 40, 50, and 60°.

2. The components have been found to interact in the methanol – dichloroethane system.

3. It has been shown that the minimum on a viscosity iotherm shifts toward the component having a higher temperature coefficient of viscosity as the temperature is raised.

LITERATURE CITED

[1] V.V.Udovenko and Ts.B.Frid, J.Phys.Chem. 22, 1263 (1948).

[2] M.I.Usanovich, J.Gen.Chem. 5, 996 (1935).

[3] V.Ya.Anosov and S.A.Pogodin. The Principles of Physicochemical Analysis, p. 158, USSR Acad. Sci. Press.

[4] O.Faust, Z. phys. Chem., 79, 97 (1912).

[5] N.N.Efremov, Bull. Inst. Phys-Chem. Analysis, 4, 1, 158 (1928).

[6] G.M.Panchenkov. The Theory of Liquid Viscosity. State Fuel Technology Press, (1947).

Received December 15, 1949.

Laboratory of Physical Chemistry
Central Asian State University

INVESTIGATION OF THE REACTION BETWEEN MALEIC ANHYDRIDE AND DIPHENYLAMINE BY THE METHODS OF PHYSICOCHEMICAL ANALYSIS

Fusibility, Viscosity, Specific Gravity, and Conductance

O. A. Osipov and Yu. V. Fedorov

Very little work has been done up to the present time on studying systems constituted by an anhydride and another anhydrous component by the methods of physicochemical analysis. Investigations of several properties of the aniline-acetic anhydride system has shown that it is a transitional system between rational and irrational ones, being closer to the former than the acetic acid – aniline system [1]. This impelled us to make a study of the reaction of an anhydride with so inactive an amine as diphenylamine. The present paper reports the results of our research on the maleic anhydride – diphenylamine system.

Substances and experimental procedure. The diphenylamine was recrystallized twice from ligroin and had a m.p. of 53.8°. The maleic anhydride was distilled at 201-202°, and then at reduced pressure. The product has a m.p. of 53.5°.

The solutions were calculated in molar per cent. The temperature at which the first crystals appeared on the cooling curve and the temperature at which the last crystals vanished on the heating curve were determined visually in a special test tube that was adequately airtight, this latter property being especially important for solutions containing a high percentage of maleic anhydride. The viscosity was measured in a viscosimeter of the closed type. To avoid the introduction of moisture when the liquid was drawn into the capillary, we used a mercury seal, which produced rarefaction [2]. The specific gravity was determined by means of a 7-ml pycnometer. The conductance of the system was measured by the Kohlrausch method. The current source was an audio-frequency generator. We used a drum bridge, with a wire 3 meters long, as the rheocord. A cell with a tight-fitting ground cover and smooth platinum electrodes was used for the measurements. The viscosity, specific gravity, and conductance were all measured in an oil thermostat, fitted with a mercury thermoregulator that enabled the temperature to be kept within ± 0.1° for long periods of time.

Fusibility. The results of our measurements of the system's fusibility are given in Table 1 and Fig. 1.

As we see from these results (Table 1), the fusibility curve has two eutectics and one sharp maximum, the first eutectic being located at 4 mol % of diphenylamine and 49.5°, and the other at 87 mol.% of diphenylamine and 46.6°. The maximum, at 113°, is located at 50 mol.% of diphenylamine, i.e., it represents

TABLE 1

Test No.	Mol. % of $(C_6H_5)_2NH$	Melting point	Test No.	Mol.% of $(C_6H_5)_2NH$	Melting point
1	0.00	53.5°	11	45.00	107.0°
2	3.97	49.5	12	50.0	113.0
3	7.84	61.0	13	55.0	109.8
4	11.18	70.1	14	65.00	99.8
5	15.48	79.0	15	70.00	92.4
6	18.86	84.2	16	80.00	78.3
7	23.13	89.0	17	85.00	58.2
8	26.07	91.9	18	88.16	46.6
9	30.00	95.0	19	96.21	50.7
10	40.00	103.0	20	100.00	53.8

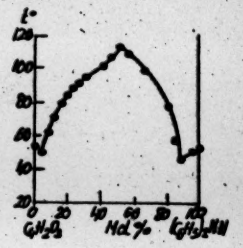


Fig. 1

a compound with the composition of $C_4H_2O_3 \cdot (C_6H_5)_2NH$. The latter fuses at a somewhat higher temperature than its separate constituents. The sharp maximum on the fusibility curve is evidence of the slight dissociation of the detected compound.

Viscosity and specific gravity. In determining the viscosity, density, and conductance at 100°, we had to work with supercooled solutions. The data on the viscosity as a function of composition at 100° and 125° are given in Table 2 and Fig. 2. The viscosity isotherms meet at an acute angle at points whose

TABLE 2

Test No.	Mol.% of $(C_6H_5)_2NH$	Density		Viscosity (centipoises)		Temperature coefficient of viscosity, (γ)
		100°	120°	100°	120°	
1	0.00	1.2593	1.2347	1.01	0.83	0.009
2	20.00	1.2415	1.1838	3.04	1.88	0.058
3	40.00	1.1905	1.1645	19.41	6.84	0.628
4	45.00	1.1694	1.1409	39.19	8.18	1.551
5	50.00	1.1601	1.1067	60.62	14.57	2.302
6	55.00	1.1133	1.0939	32.52	6.89	1.282
7	60.00	1.1024	1.0782	16.01	6.35	0.483
8	80.00	1.0731	1.0527	3.03	1.82	0.061
9	100.0	1.0281	1.0042	1.59	1.13	0.023

abscissas are those of the resultant compound. The viscosity drops steeply as the temperature is raised, though the position of the maximum along the composition axis remains unchanged. The great divergence between the viscosity isotherms in the region of the equimolar solution indicates the high temperature coefficient at these concentrations. The absolute temperature coefficient curve (Table 2, upper curve in Fig. 2) has an even sharper maximum at 50 mol.% of diphenylamine than the isotherm of the property itself. Hence, the nature of both the viscosity isotherm and the temperature coefficient curve is evidence of the formation of an undissociated compound with the composition of $C_4H_2O_3 \cdot (C_6H_5)_2NH$ in the system.

The behavior of the system's specific gravity is somewhat different. The measurement results of this property at 100 and 120° are given in Table 2 and Fig. 2. The specific gravity curves are slightly concave toward the composition axis, indicating comparatively slight shrinkage when the constituents interact.

Conductance. The results of our conductance measurements at 100 and 120° are given in Table 3 and Fig. 3. The conductance isotherms traverse two maxima, the first maxima being located at 20 mol. % of diphenylamine; it is more pronounced at 120° than at 100°. A distinct, sharp minimum is located at 50 mol.% of diphenylamine, corresponding to the composition of the compound. The second maximum lies at 55-60 mol.% of diphenylamine and is much less pronounced than the first.

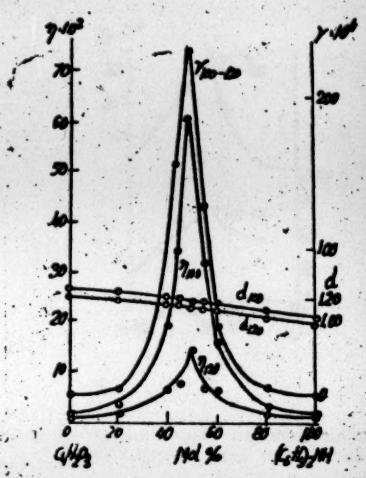


Fig. 2.

According to the classification of conductance isotherms of binary liquid systems [3,4], these isotherms are those of rational systems..

If we eliminate the influence of viscosity upon conductance, i.e., if we calculate the corrected conductance from the simple formula $\varkappa \cdot \eta = \varkappa_{\text{corrected}}$, we get the results given in Table 3 and Fig. 4 (for 120°. As we see, the curve of corrected conductance passes through a singular maximum, corresponding to the equimolecular composition of the constituents. The appearance of a singular maximum on the curve of corrected conductance likewise indicates the formation of an undissociated compound within the system. The curve of the relative temperature coefficient as a function of the composition likewise passes through a singular maximum, located at 50 mol.% of diphenylamine.

TABLE 3

Test No.	Mol.% of $(C_6H_5)_2NH$	Conductance, $\varkappa \cdot 10^6$		Corrected conductance, $\varkappa \cdot \eta \cdot 10^6$		Temperature coefficient, $\alpha \cdot 10^6$
		100°	120°	100°	120°	
1	0.00	9.56	12.84	9.68	10.69	0.015
2	20.00	42.62	80.66	129.73	151.47	0.031
3	30.00	32.26	68.51	–	–	
4	40.00	13.36	39.79	259.26	272.15	0.049
5	45.00	10.56	35.20	414.10	292.93	0.054
6	50.00	7.11	25.17	431.18	348.90	0.056
7	55.00	10.20	28.10	331.65	193.57	0.047
8	60.00	10.31	25.71	164.80	163.32	0.043
9	70.00	3.36	10.38	–	–	
10	80.00	2.14	4.56	6.50	8.30	0.036
11	100.00	0.32	0.35	0.52	0.77	0.0033

Evaluation of results. Our findings on the viscosity, fusibility, and conductance indicate that the constituents of our system interact chemically to form an undissociated compound in the liquid phase with the composition of $C_4H_2O_3 \cdot (C_6H_5)_2NH$, manifested as singular points on the diagrams of the foregoing properties. The results of our calculations of the temperature coefficients of viscosity and conductance, as well as of the corrected conductance, corroborate our assumptions.

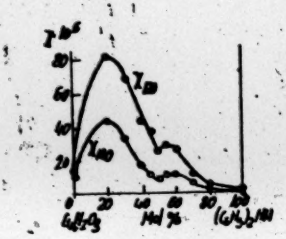


Fig. 3.

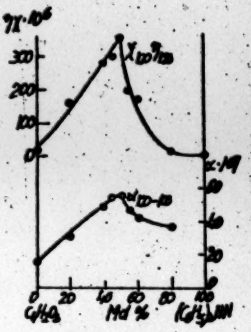


Fig. 4.

Hence, the fusibility, conductance, and viscosity curves indicate that the maleic anhydride – diphenylamine system is a rational one, while the specific gravity isotherm classes it as an irrational one. It must be remembered, however, that the specific gravity isotherm is not a typical one, inasmuch as the magnitude of the latter varies only slightly, and it is hard to make out the singular point.

SUMMARY

1. A study has been made of the fusibility, viscosity, specific gravity, and conductance of the maleic anhydride – diphenylamine system.

2. It has been proved that a compound of the composition $C_4H_2O_3 \cdot (C_6H_5)_2NH$ is formed in this system.

3. The temperature coefficients of viscosity and conductance have been calculated, and the corrected conductance has been computed.

4. It has been shown that the fusibility, viscosity, and conductance findings all class this system as a rational one.

LITERATURE CITED

[1] M.A.Klochko and O.P.Chanukvadze, Bull. USSR Acad. Sci., Div. Chem. Sci., 1947, 585.

[2] M.A.Klochko, Bull. USSR Acad. Sci., Div. Chem. Sci., 1937, 641.

[3] N.A.Trifonov, Bull. Biological Research Institute, Perm State Univ., 6, No. 5, 247 (1938).

[4] N.S.Kurnakov, Introduction to Physicochemical Analysis, 4th ed., p. 342. Moscow-Leningrad (1940).

Received October 2, 1949.

Laboratory of Physical Chemistry,
V.M.Molotov State University,
Rostov-on-Don

TRANSFORMATIONS OF HYDROCARBONS WITH OXIDE CATALYSTS

III.* The Role of Various Transformations in the Aromatization of Paraffin And Olefin Hydrocarbons by Chrome Catalysts

R. D. Obolentsev and Yu. N. Usov

The aromatization of aliphatic hydrocarbons with chrome catalysts continues to attract the atention of numerous research workers. The published papers dealing with the comparative importance of the various kinds of transformations cover, however, only research into the mechanism of the contact transformation of heptane at a vanadium catalyst, as performed by Plate and Tarasova [1].

The only paper on the kinetics of the aromatization reactions of aliphatic hydrocarbons with chrome catalysts is the paper by Karzhev and Sorokin [2].

Interesting in conception, this research gives rise to doubt concerning the experimental procedure employed and the working up of the results secured. With a catalyst bed 25 cm long, for example, the temperature was measured at only one point, while no block was used to even out the temperature. The platinum – platinum-rhodium thermocouple employed by the authors did not afford the necessary precision of measurement of temperature, while the supply of hydrocarbons from an ordinary buret could not ensure the required constancy of the rate of supply of the vapor to the reaction chamber.

The waste heptane was not analyzed during aromatization, though the weight of a liter of the gas (calculated by us from their test data) proved to be approximately 0.7 g, proving that appreciable cracking had occurred. The balance sheet shows no coke, though the authors themselves write that "when the pieces of catalyst were broken apart deposits of carbon particles were observed inside them."

The authors determined the kinetic state of affairs by comparing the constants of action.

They assert that the constants were calculated from the equation for a monomolecular reaction: $K = \frac{2.3}{\tau} \log \frac{a}{(a - x)}$, where τ is the contact time in minutes, $(a - x)$ is the percentage of the hydrocarbon reacted, and a is the percentage of the initial hydrocarbon.

The discrepancy of some 30% between the constants of action for about the same contact times did not entitle the authors to consider the reaction a first-order one. Still, the authors, commenting that "this reaction must be regarded as a monomolecular one," calculated the activation energy $E_{app.}$ from the Arrhenius equation, finding it to be 35,800 cal/mol for the cyclization of n-heptane.

Our calculations, based on the authors' experimental data, with $(a - x)$ taken as the percentage of the unreacted heptane, as it should be, and a as 100%,

---

* Cf. J. Gen. Chem. 18, 553 (1948); 17, 897 (1947).

yielded values of the constants that differed from those secured by Karzhev and Sorokin. The variation of the logarithms of these constants with temperature (Fig. 1, Curve 5) did not follow Arrhenius' equation.

We also used the Karzhev and Sorokin data on the yield of aromatics and gas to compute the apparent activation energy of the aromatization reaction, $E_{app.}$ = = 32,400 cal/mole; for the "reaction of overall dehydrogenation" $E_{app.}$ = 35,200 cal/mole, according to the data of some experiments, and 27,400 cal/mole, according to others (Fig. 1), while the authors give the apparent activation energy of the cyclization reaction as $E^{IV}_{app.}$ = 35,800 cal/mole. This value is secured for the straight line IV passing through the points 1 and 3; if the straight line is passed through the points 1 and 2, $E^{IV}_{app.}$ = $\simeq$38,000 cal/mole. The value of $E_{app.}$ of the aromatization reaction we have calculated from the Karzhev and Sorokin data is lower than the $E_{app.}$ for the "overall dehydrogenation reaction," which

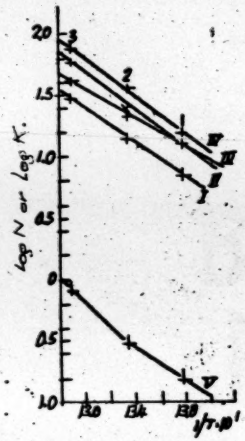


Fig. 1. Variation of log K and of the logarithms of N, the extent of conversion, with temperature in the aromatization and the "overall dehydrogenation" of n-heptane, according to the experimental data of Karzhev and Sorokin [2]

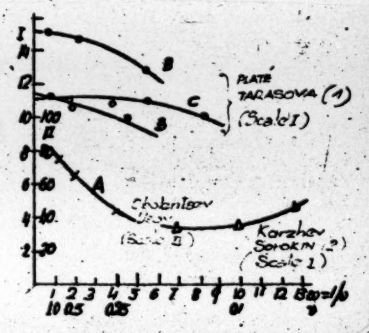


Fig. 2. Variation of the mean reaction rate of the "overall dehydrogenation" of n-heptane with contact time at a temperature of 480°.

contradicts the findings of Plate and Tarasova and our own (cf the experimental section below), according to which the apparent activation energy of the aromatization of n-heptane is much higher than that for the overall dehydrogenation reaction.

Inspection of the curves in Fig. 2 shows that the mean reaction rate of the process of overall dehydrogenation rises somewhat with increasing contact time, according to the data of Karzhev and Sorokin. If the overall dehydrogenation were described by a first-order equation, the mean rate at which the gas is formed ought to decrease as the time of contact rises. In view of the long contact times employed in the Karzhev and Sorokin experiments, it must be assumed that the mean rate of evolution of hydrogen was masked by the mean rate of evolution

of the gaseous products of the cracking of the heptane.

The foregoing leads us to think that the conclusion of Karzhev and Sorokin that "the conversion of n-heptane with a chrome catalyst at atmospheric pressure in the temperature range of 450-500° is of the first order, kinetically" is not borne out by their own experimental data, nor is their value of 35,800 cal/mole for the apparent activation energy.

In passing, we might mention the extremely low activity and the absence of the required selectivity in the catalyst employed by Karzhev and Sorokin.

We have commented on the Karzhev and Sorokin paper in as much detail as possible within the framework of this paper, since it is the only published paper on the kinetics of the aromatization of n-heptane with a chrome catalyst, being used as a reference source up to the present time [1,3].

Figure 2 indicates that the Plate and Tarasova vanadium catalyst was much more active, though this catalyst is far from resembling, even as a first approximation, the modern aromatizing catalysts, as is seen from a comparison of the Curves B and A of Plate and Tarasova and Obolentsev and Usov, respectively.

The effect of contact time upon the mean rate of the overall dehydrogenation reaction was plotted by Plate and Tarasova in the following coordinates: mean reaction rate versus rate of supply of the raw material, the dimension thus being [sec.$^{-1}$]. Our recomputation of the data cited by Plate and Tarasova, plotted in Fig. 2 in the usually adopted coordinates, with the mean rate $\omega = \frac{1}{\tau}$, where τ is the volumetric rate of flow, i.e., the dimension of ω is [sec.], shows that the results of their experiments do not furnish an unequivocal answer to the question of how the aromatization process varies with the time of contact. Though this did not prevent the authors from determining the activation energy of the contact conversions of n-heptane with a vanadium catalyst, the problem of the order of aromatization reactions with oxide catalysts remained moot.

We might also mention the paper by Pitkethly and Steiner [4] at this point, as they investigated the variation of the concentration of the "aromatic" and of the olefins in the catalyzate of n-heptane with the time of contact. Unfortunately, the authors' paper does not give the material balance of their experiments, so that we cannot determine the yield of the "aromatic" and of the unsaturated hydrocarbons in terms of the initial heptane. Figures 3 and 10 reproduce curves from the Pitkethly and Steiner paper, replotted to our scale. In view of the fact that the yield of liquid products drops off with increasing extent of transformation of the n-heptane, or putting it otherwise, with an increase in the contact time, it must be remembered that substituting a "per cent yield" ordinate for a "per cent content" ordinate involves a certain change in the position of the curves.

Our curves closely resemble the curves plotted from the Pitkethly and Steiner data (Fig. 3). The explanation given by Pitkethly and Steiner for their alleged observation of a constant heptene concentration as being due to the rate at which it was formed from the heptane equaling the rate of its conversion into toluene is unfounded.

Heptene is a by-product, and not an intermediate product of the aromatization of heptane with a chrome catalyst (cf the experimental section for details).

EXPERIMENTAL

We used the following substances as initial raw materials: n-heptane; 2,2,4-trimethylpentane; heptene-1; 2-methylhexene-2; and 3-methylheptene-3; we have reported on their synthesis earlier. The experimental procedure and the catalyst used were likewise the same as before [5].

The chrome catalyst we employed retained practically constant activity throughout the run, i.e., the quantity of gas evolved was directly proportional to the length of the run.

The waste gas produced during aromatization was analyzed by means of a gas analyzer, using the method described by the "Khimgaz" Institute [6]. The analysis results are given in Table 1. The gaseous products of the tests on the

TABLE 1

Composition of the Waste Gas in the Aromatization of Paraffin and Olefin Hydrocarbons

Test No.	Initial hydrocarbon	Temperature, (°C)	Composition of the gas, % by volume				
			H_2	C_nH_{2n+2}	C_2H_4	$n\text{-}C_4H_8 + C_3H_6$	$iso\text{-}C_4H_8$
45	n-Heptane	450	78.5	14.4	–	7.1	–
46		480	83.9	11.2	–	4.9	–
47		510	85.9	11.0	–	3.0	–
52	Isooctane	480	74.5	7.5	–	18.0	–
53		510	56.5	22.2	0.4	5.0	15.9
76	Heptene-1	450	80.2	14.8	1.1	3.6	0.3
77		480	77.0	15.4	1.2	6.2	0.2
78		510	74.2	18.3	1.2	6.1	0.1
59	2-Methyl-hexene-2	450	76.0	13.8	2.2	5.8	2.2
60		480	73.8	12.7	3.0	7.3	3.2
61		510	67.1	20.4	2.4	6.3	3.8

aromatization of heptane were rectified with a Podbielniak tower, the total hydrogen + methane ranging from 84 to 98%. In the light of this fact, we estimated the mean rate of the "overall dehydrogenation" of heptane, heptene-1, and 2-methylhexene-2 from the volume of gas evolved. The justification for this procedure has been given in the paper by Plate and Tarasova [1]. At a constant rate of supply of the initial raw material to the reactor, i.e., for a given contact time, the mean rate at which the gaseous products were evolved remained practically constant in all the tests run by us. Hence, no matter whether the reaction obeyed the equation for a zero-order or first-order reaction, the mean reaction rate can be employed, for a constant time of contact, to calculate the apparent activation energy. Many authors of papers on the aromatization of hydrocarbons [1,7] have used the mean reaction rate in computing the apparent activation energy. In order to facilitate comparison of our results, we also used the mean rate to compute the apparent activation energy, the temperature coefficient of the aromatization reaction, the formation of coke and gas, the "overall dehydrogenation", and the overall extent of conversion of the heptane, 2,2,4-trimethylpentane, 2-methylhexene-2, and heptene 1.

A. Effect of contact time upon the conversion of n-heptane and 2-methylhexene-2 with a chrome catalyst

Curve A in Fig. 2 represents the mean rate at which gaseous products are evolved in the aromatization of heptane as a function of the fictitious contact time ω. The mean rate may be taken as approximately inversely proportional to the contact time for the interval ω = 1-4; we have plotted the analogous, though less pronounced, curves B and C from the experimental data of Plate and Tarasova [1]. Unfortunately, the data cited by these authors leave considerable room for

choice, so that Moldavsky considered Plate and Tarasova to have proved the reaction to be a zero-order one, evidently on the basis of the data represented by Curve C. In our opinion, the practically constant value of the mean rate at which the gaseous products are evolved is due in this case to the fact that the overall yield of aromatic and unsaturated hydrocarbons is given approximately by a straight line in the ω = 1-4 range in the kinetic graphs (Figs. 3 and 10). This approximation of sections of the curve to a straight line does not justify us, however, in classing aromatization as a zero-order reaction. Most likely, because of this Plate and Tarasova [1] came to no conclusion regarding the apparent order of the aromatization reaction.

Tables 2 and 3 and Fig. 3 give the results of our observations during the aromatization of n-heptane and 2-methylhexene-2 on the variation of the yield of the aromatic and unsaturated hydrocarbons with the true contact time at the temperature of 480°. At 480° the transformation of heptane into toluene is irreversible, the equilibrium extent of conversion of heptane into heptene being 28% [3]. Examination of Tables 2 and 3 discloses that the extent of conversion of heptane into aromatic and unsaturated hydrocarbons is stabilized at about 15 and 8%, respectively, that is, it never reaches the equilibrium value.

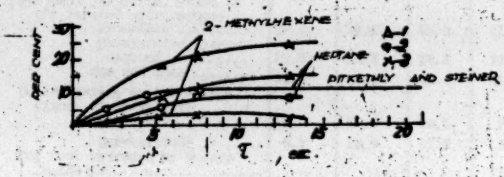


Fig. 3. Extent of conversion of heptane and 2-methylhexene-2 into aromatic and unsaturated hydrocarbons as a function of the time of contact.

1 – aromatics; 2 – unsaturated; 3 – paraffin.

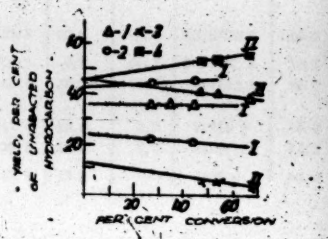


Fig. 4. Yields of aromatic, unsaturated, and paraffin hydrocarbons, plus the total gas and coke, extrapolated to zero conversion of n-heptane and 2-methylhexene-2.

1 – Aromatic; 2 – unsaturated; 3 – paraffin; 4 coke and gas; I – heptane; II – 2-methylhexene-2

Figure 4 gives the curves for the yields of aromatic, unsaturated, and paraffin hydrocarbons, together with the total gas and coke, extrapolated to zero conversion. Extrapolation to zero has often been used by various researchers to establish the primary reactions [8]. Inspection of the straight lines at zero conversion indicates that the reactions of aromatization, dehydrogenation, and hydrogenation, and the formation of coke and gas all occur simultaneously and parallel to one another.

The yield of aromatic hydrocarbons remains constant, in terms of the reacted heptane, up to 45% conversion, whereas the yield of the unsaturated hydrocarbons drops off somewhat, about as much as the yield of coke and gas rises. It must be assumed that some of the unsaturated hydrocarbons are depolymerized, giving rise to a small quantity of gaseous olefin hydrocarbons. Most of the gaseous paraffin hydrocarbons contained in the waste gases consists of methane.

The amount of hydrogen evolved greatly exceeds the calculated amount, which

Experimental data	Heptane				Heptane		2,2,4-Trimethylpentane		
	Constant time, sec (t = 480°)				Temperature, °C ω = 2		Temperature, °C ω = 2		
	5.3	7.5	13	450	480	510	450	480*	510
Mols passed through	0.0435	0.0544	0.0476	0.0455	0.0475	0.0475	0.0475	0.0475	0.0475
Calculated quantity of Hydrogen, ml	405	714	785	189	564	1622	153	336/350	761
Gas evolved, ml at NTP	805	1050	1230	294	945	2590	146	434/497	1225
inclusive of hydrogen, ml at NTP	–	–	–	231	793	2222	–	324/ –	686
Ratios: a) Hydrogen evolved: Calcd. amt. hydrogen	–	–	–	1.22	1.40	1.37	–	0.96/ –	0.90
b) Gas evolved: calcd. amt. of hydrogen	1.49	1.47	1.57	1.55	1.68	1.59	0.96	1.29/1.41	1.61
Per cent converted, based on hydrocarbon passed through	26.8	35.4	45.0	20.3	36.3	71.9	15.5	28.7/28.9	51.6
Including: aromatics	9.5	12.5	16.2	2.5	10.6	36.4	2.0	5.4/5.9	15.2
Unsaturated hydrocarbons	5.6	8.6	8.8	8.5	10.6	7.0	6.4	10.0/9.4	10.7
Gas and coke	11.7	14.3	20.0	9.3	15.1	28.5	7.1	13.3/13.6	25.7
Per cent converted, based on the reacted hydrocarbon:									
Aromatics	35.4	35.3	36.0	12.3	29.3	50.6	12.9	18.8/20.4	29.5
Unsaturated hydrocarbons	20.9	24.3	19.6	41.8	29.3	9.7	41.2	34.8/32.5	20.8
Gas and coke	43.7	40.4	44.4	45.9	41.4	39.7	45.9	6.4/47.1	49.7
Concentration in the catalyzate, % by weight:									
Aromatics	10	13.6	19.0	2.5	11.6	49.0	2.0	5.7/6.5	19.0
Unsaturateds	6.3	10.0	11.0	9.1	12.5	10.0	7.0	12.8/11	10.1
Per cent hydrogen by volume in the gas	–	–	–	78.5	83.9	85.9	–	74.5 –	56.0

	2-Methylhexene-2				Heptene-1				
Mols passed through	0.0455	0.0475	0.0476	0.0417	0.0417	0.0340	0.0345	0.0345	0.0345
Calculated quantity of hydrogen, ml	565	662	810	370	612	860	360	702	1189
Gas evolved, ml at NTP	990	1200	1730	480	1020	1690	500	1200	2458
Inclusive of hydrogen, ml at NTP	–	–	1140	365	756	1130	402	925	1818
Ratios: a) Hydrogen evolved: calcd. amount hydrogen	–	–	1.41	1.00	1.23	1.32	1.11	1.31	1.52
b) Gas evolved: calcd. amount hydrogen	1.75	1.81	2.13	1.30	1.67	1.97	1.38	1.71	2.06
Per cent converted based on hydrocarbon passed through	47.8	54.4	66.7	33.7	55.6	81.1	38.9	70.1	98.8
Including: aromatics	19.5	21.8	26.1	13.5	23.0	38.3	16.0	32.6	52.5
unsaturateds	2.9	3.4	2.2	0.8	3.5	2.2	1.5	6.9	2.9
gas and coke	25.4	29.2	38.4	19.4	29.0	40.6	21.4	30.6	41.4
Per cent converted, based on the reacted hydrocarbon:									
aromatics	40.7	40.1	39.2	40.2	41.4	47.3	41.2	46.4	54.2
unsaturateds	6.1	6.2	3.3	2.4	6.3	2.7	3.9	9.9	3.0
gas and coke	53.2	53.7	57.5	57.4	52.3	50.0	54.9	43.7	42.8
Concentration in the catalyzate, % by weight:									
aromatics	25.0	29.5	41.0	16.0	31.1	63.0	20.0	45.4	58.8
unsaturateds	4.0	5.0	3.7	1.0	5.2	3.9	2.4	10.4	5.3
Per cent hydrogen by volume in the gas	–	–	66.0	76.0	73.8	67.1	80.2	77.9	74.2

* Data of two parallel tests

we determined on this basis: the formation of one mole of an aromatic from one mole of a saturated hydrocarbon involves the evolution of 4 moles of hydrogen, the corresponding figure being 3 moles in the case of an unsaturated hydrocarbon; 1 mole of hydrogen is liberated or absorbed in the formation of one mole of unsaturated or saturated hydrocarbons; and lastly, that if demethylation takes place instead of dehydrogenation of the heptane and the isooctane, the "calculated" quantity of hydrogen does not change, inasmuch as the aggregate volume of the methane plus the hydrogen is equivalent to the "theoretical volume" of the hydrogen. In the aromatization of heptane the ratio of the volume of gas evolved to the calculated quantity of hydrogen rose from 1.49 to 1.57 when the contact time was increased from 5.3 sec to 13 sec, i.e., increasing the contact time has the same effect as raising the temperature from 450 to 510° (Table 2).

Table 3 and Figs. 3 and 4 contain the data showing the conversion of 2-methylhexene-2 as a function of the time and percentage of conversion. These figures resemble those for heptane. 2-Methylhexene-2 is converted in parallel into aromatic and saturated hydrocarbons, as well as into coke and gas. The participation of the unsaturated hydrocarbons in the formation of gas and coke is shown more strikingly (Curves II). At first glance, the extent to which the conversion of 2-methylhexene-2 into aromatic hydrocarbons depends upon the time of contact appears to be the same as in the case of heptane. The conversion of 2-methylhexene-2 into aromatics (in terms of the reacted initial hydrocarbon) is somewhat higher than that of heptane: 40% as against 35%, but as the extent of conversion increases, the yield of aromatics drops; the conversion into coke and gas is much higher, being 53-67% as against 43% for heptane, which may be due to the partial conversion of the aromatics into coke. The formation of saturated hydrocarbons is of particular interest, this conversion tending to increase as the contact time is shortened (Curve II). That is probably why the cracking of the newly formed paraffin hydrocarbons, and their conversion into aromatics parallels the aromatization of 2-methylhexene-2. The amount of hydrogen evolved in the aromatization of 2-methylhexene-2 is about 40% higher than the calculated quantity, i.e., it confirms the observation we made in the aromatization of heptane.

Our experiments on the aromatization of 2-methylhexene-2 and n-heptane have shown that the principal transformations that take place simultaneously in the presence of a chrome catalyst at 480° are the formation of aromatics and of coke. The side reactions, occurring parallel to the main ones, are the formation of olefin hydrocarbons in the case of heptane and of paraffin hydrocarbons in the case of 2-methyl-hexene-2.

We get the impression that there are various types of catalyst surface. Then the destruction of the portions of the surface that are specific for cracking ought to increase the selectivity of the catalyst's action. We know that chrome catalysts acquire high selectivity after several runs with subsequent regeneration. Under comparable conditions, the aromatization of the same substance with chrome catalysts that have about the same surface but have been prepared in different ways yields a catalyzate containing aromatic and unsaturated hydrocarbons in various proportions, while the gas consists of 99% hydrogen or 80% and less. These well-known facts confirm the conclusion that a chrome catalyst has surfaces of different kinds, and they make quite understandable the need for forming the surface by running the catalyst through a cycle of operations before it is placed in continuous operation.

B. Effect of temperature upon the conversion of n-heptane, heptene-1, 2-methylhexene-2, and 2,2,4-trimethylpentane with a chrome catalyst

The experiments on the aromatization of n-heptane, heptene-1, 2-methylhexene-2, and 2,2,4-trimethylpentane were run at 450 and 510°, the volumetric rate

of flow of the raw material into the reactor being kept constant at 0.5, i.e., the contact time was not strictly constant owing to the different percentage conversion. But, as we have indicated above, at a given constant temperature this circumstance ought not to affect the proportions of the resultant products very much (Fig. 3). The results of these tests are given in Tables 2 and 3 and in Figs. 5, 6, 7, and 8.

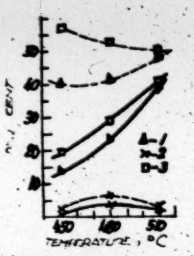


Fig. 5. Conversion of 2-methylhexene-2 with a chrome catalyst.

1 – Aromatics; 2 – paraffins 3 – total coke and gas. Solid lines – 2-methylhexene-2 passed through; broken lines – reacted 2-methylhexene-2.

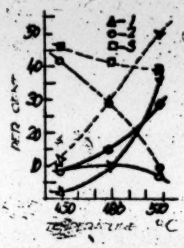


Fig. 6. Conversion of n-heptane with a chrome catalyst.

1 – Aromatics; 2 – paraffins; 3 – total coke and gas. Solid lines – n-heptane passed through; broken lines – reacted n-heptane.

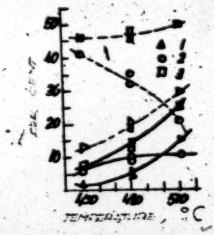


Fig. 7. Conversion of isooctane with a chrome catalyst.

1 – Aromatics; 2 – paraffins; 3 – total coke and gas; Solid lines – isooctane passed broken lines – reacted isooctane.

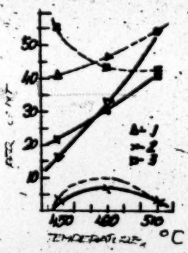


Fig. 8. Conversion of heptene-1 with a chrome catalyst.

1 – Aromatics; 2 – paraffins; 3 – total coke and gas; Solid lines – heptene-1 passed through; broken lines – reacted heptene-1.

The percent conversion of heptane into coke and gas drops 6% as the temperature is raised from 450 to 510°, the $\frac{\text{actually evolved hydrogen}}{\text{'computed' amount of hydrogen}}$ ratio rising from 1.22 to about 1.4.

Similar behavior was found to prevail in the aromatization of heptene-1 and

2-methylhexene-2. In the case of 2,2,4-trimethylpentane, the per cent conversion into coke and gas rose somewhat. The increase in the ratio of the evolved hydrogen to the computed quantity was about 15% for heptane, and about 35% for heptene-1 and 2-methylhexene-2. Raising the temperature from 450 to 510° approximately doubled the per cent conversion into coke and gas for heptene-1 and 2-methylhexene-2, and approximately tripled it for n-heptane and 2,2,4-trimethylpentane, although the yield of coke and gas was higher in absolute terms for the heptenes at equal temperatures.

We know that, in contrast to the equilibrium percentage of conversion, the practical completeness of a reaction increases with rising temperatures both for endothermic and for exothermic reactions. Only two kinds of reactions can participate in the formation of coke: 1) cracking – alkylation; and 2) dehydrogenation – hydrogenation, i.e., endothermic as well as exothermic reactions. In the aromatization of heptenes, the temperature coefficients of the reaction rate of coke and gas formation are lower than for heptane and isooctane (Table 4). We

TABLE 4

Apparent energy of activation $E_{app.}$ and the temperature coefficients of the reaction rate (K_t) at temperature intervals of 450-510°.

Process	Initial hydrocarbons			
	Heptane	2,2,4-trimethylpentane	2-Methylhexene-2	Heptene-1
$E_{app.}$ of the aromatization reaction	41200	38200	19700	22500[1]
K_t of same	1.48	1.44	1.21	1.24
E_{app} of the process involved in the formation of coke and gas	20000[3]	24400	14000	13000[2]
K_t of same	1.21	1.26	1.14	1.13
$E_{app.}$ of the overall conversion of the initial hydrocarbon	23800[4]	22500	16900	?[5]
K_t of same	1.26	1.24	1.18	?[5]
$E_{app.}$ of the overall hydrogenation reaction	39800	39800	27000	29700
K_t of same	1.42	1.42	1.29	1.3

Note: The extreme values of the activation energy were: 1) 21.7 – 25.1; 2) 12.5 – 13.8; 3) 17.3 – 20.4; 4) 21.8 – 24.8; 5) The log of the overall per cent conversion is not a linear function of 1/T.

attribute this preponderance in the formation of coke to reactions of the first type, which result in the formation of high-polymer polyene hydrocarbons. The increase in the evolution of excess hydrogen over the "calculated" figure does not contradict the preponderance of alkylation reactions, inasmuch as the dehydrogenation reaction rate increases as the temperature rises. The temperature coefficients of the reaction rates for the reactions involved in the formation of coke and gas are somewhat lower than the corresponding temperature coefficients for the reaction rates of aromatization (Table 4). The curves that represent the variation of the percent conversion of n-heptane and isooctane into unsaturated hydrocarbons with temperature all pass through maxima, though the latter are not very prominent, to be sure. The passage through a maximum when plotted on

the coordinates: per cent conversion versus temperature should be due to the consecutive formation of olefin hydrocarbons, according to Plate and Tarasova [1]. We demonstrated above that the variation of the per cent conversion of n-heptane and 2-methylhexene-2 with time indicates the parallel formation of aromatic, unsaturated, and paraffin hydrocarbons, in addition to coke. We therefore believe that the passage of the curves of olefin hydrocarbons through maxima in Figs. 6 and 7 is due to the comparatively low temperature coefficient of the reaction involved in their formation as well as to the conversion of the olefin hydrocarbons into coke and gas.

The curves in Fig. 6 that show the conversion of n-heptane into "aromatics" coke, and gas with a chrome catalyst are like the analogous curves in the paper by Plate and Tarasova [1], whereas the curves for the conversion of n-heptane into unsaturated hydrocarbons are quite different.

Our results indicate that there is not much difference between the types of conversion undergone by unsaturated hydrocarbons (heptene-1 and 2-methylhexene-2). As the temperature rises, the per cent converted into aromatic hydrocarbons drops, while the per cent converted into coke and gas increases. The overall per cent conversion rises with rising temperature, the curve that represents the conversion of the olefins into paraffin hydrocarbons passing through a maximum like that on the curve for the olefin hydrocarbons in the experiments on the aromatization of heptane. This passage through a maximum is due to secondary reactions involved in the conversion of the paraffin hydrocarbons. To judge by Fig. 4, the paraffin hydrocarbons are converted into aromatics, coke, and gas.

It follows from the foregoing that the per cent conversion into coke is 40-60% for the olefin and paraffin hydrocarbons we have investigated in the temperature range of 450-510°, with a chrome catalyst, and at a constant volumetric rate of flow $v = 0.5$. For the unsaturated hydrocarbons the per cent conversion into aromatics is 40-55%, while it ranges from 10 to 50%, depending upon the structure, for the paraffin hydrocarbons.

It should be said at this point that highly branched paraffin hydrocarbons are cracked much more readily than the isomeric paraffins of normal structure; the yield of coke and gas, in terms of the converted initial hydrocarbon, rises with rising temperature in the aromatization of isooctane, whereas it falls in the aromatization of heptane (Figs. 6 and 7).

EVALUATION OF RESULTS

The variation of the per cent conversion of n-heptane and 2-methylhexene-2 is in good agreement [12] with the equation proposed by Burlakov and Kazeev [13]:

$$\ln \frac{D}{D - M} = a \cdot \tau^b, \qquad (1)$$

where M is the per cent conversion; D is the maximum per cent conversion; τ is the time of contact; a and b are the equation parameters, a being a constant characterizing the magnitude of the reaction rate, and b characterizing the type of reaction and, together with the exponential, determining the process rate.

From the data in Table 2 we have calculated that the conversion of heptane into an aromatic at 480° is described by the equation:

$$\ln \frac{17}{17 - M} = 0.097 \cdot \tau^{1.2} \qquad (2)$$

whereas the conversion of 2-methylhexene-2 into an aromatic (as given by the data in Table 3) is described by the equation:

$$\ln \frac{35}{35 - M} = 0.303 \cdot \tau^{0.54}. \qquad (3)$$

Figure 10 gives the "theoretical curves" plotted from Equations (2) and (3). The experimental points are in good conformity with the computed curves.

Examination of Fig. 10 and Equations (2) and (3) indicates that the maximum conversion of the paraffin hydrocarbon (heptane) at the given temperature is half the maximum conversion of the olefin hydrocarbon (2-methylhexene-2). The heptane and 2-methylhexene-2 curves diverge greatly at short contact times (up to 4-5 seconds). The shape of the heptane curve indicates that the reaction in which the "aromatics" are formed is preceded by an induction period. This conclusion is corroborated by the value of $\underline{b} = 1.20$, i.e., $\underline{b} > 1$, which is typical of reactions having an induction period [13]. It will be remembered that Hugh, on the basis of general (in our opinion wrong) considerations concerning the consecutiveness of the aromatization of paraffin hydrocarbons, asserted in the discussion of the Pitkethly and Steiner report [4] that the equation;

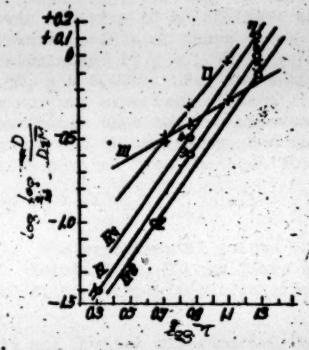


Fig. 9. Equation anamorphoses.

2, 3 – The present research; 4 – 4 – Pitkethly and Steiner.

$$\frac{d[Ar]}{d\tau} = 0, \qquad (4)$$

where [Ar] is the aromatic concentration, and τ is the contact time, must hold good in the region of extremely brief contact times.

Inspection of Equations (2) and (4) indicates the erroneous nature of this conclusion, since the aromatic concentration continues to rise even in the region of short contact times, even though it is retarded.

The parameter $\underline{a}$ for the aromatization of heptane is one third the size of the same parameter for the aromatization of 2-methylhexene-2, i.e., rate of aromatization of the olefin hydrocarbon C_7H_{14} is much higher than that of heptane, C_7H_{16}. The aromatization of 2-methylhexene-2 requires no induction period and has a parameter $\underline{b} = 0.54$, which is close to the typical $\underline{b} = 0.53$ for bimolecular reactions [13].

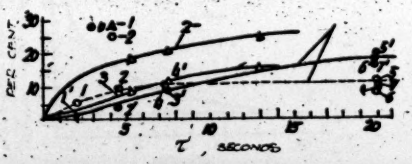


Fig. 10. Curves of the conversion of heptane and 2-methylhexene-2 as functions of time, plotted from Equations (2) and (3).

1 – Aromatics; 2 – unsaturated hydrocarbons.

Many authors [8,9,11] cite the passage in the paper by Pitkethly and Steiner in which the American authors state that the practical constancy of the $C_7H_{14}:C_7H_{16}$ ration at 0.12 to 0.17 is allegedly due to the conversion of heptene into an "aromatic" at a rate equaling the rate of its formation from heptane.

We have used the experimental data cited by Pitkethly and Steiner to plot the

anamorphoses IV, IVa, and IVb shown in Fig. 9.

It is quite obvious that neither Pitkethly and Steiner nor the subsequent research workers who have cited them drew the correct conclusions from the experimental findings. In various tests (numbered 1-7 in our list), the Pitkethly and Steiner catalysts did not possess constant activity; to be more precise, the tests fall into 3 groups, depending upon the value of a: I – Tests No. 4,7; II – Tests No. 1, 3, 6; and III – Tests No. 2, 5. Naturally, the type of reaction cannot vary, depending upon the higher or lower activity of a catalyst; accordingly, the straight lines on which the experimental points of these three groups lie are parallel to one another; we have calculated: 1) b = 1.42, a = = 0.0412; 2) b = 1.413, a = 0.0338; and 3) b = 1.38, a = 0.0281. For the sake of comparison we plotted the anamorphosis II from our own experimental data: [Equation (2)]. Comparison of the anamorphoses indicates that the aromatization reaction is of the same type in Pitkethly and Steiner and in our tests, but that the catalyst we employed was more active. The curve plotted from the equation:

$$\ln \frac{20}{20 - M} = 0.0338 \cdot \tau^{1.41} \qquad (4)$$

is reproduced in Fig. 10 (anamorphose IV, Fig. 9). The experimental points 1, 3, and 6 lie beautifully in the calculated curve. Points 2, 4, 5, and 7 are somewhat off, owing to the defect in the Pitkethly and Steiner experiments referred to above.

According to our calculation of the Pitkethly and Steiner experimental data the conversion of heptane into olefins is governed by the following equation:

$$\ln \frac{12}{12 - M} = 0.290 \tau^{1.02} \qquad (5)$$

The dotted line in Fig. 10 has been plotted from this equation.

Examination of the ratio $\frac{\text{concentration of unsaturated hydrocarbons}}{\text{concentration of aromatic hydrocarbons}}$ indicates that it drops from 4 to 0.71 within the contact time 1 to 15 seconds (Fig. 11). Hence, there can be no question of any constancy of the heptane concentration, such as was allegedly observed by Pitkethly and Steiner. To judge by the results of our

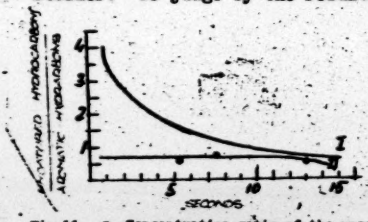


Fig. 11. I. Concentration ratio of the unsaturated to aromatic hydrocarbons in the aromatizate of n-heptane (Pitkethly and Steiner)

II: $\frac{\text{Percent conversion of } C_7H_{16} \text{ into unsaturated hydrocarbons}}{\text{Percent conversion of } C_7H_{16} \text{ into aromatic hydrocarbons}}$ (present research)

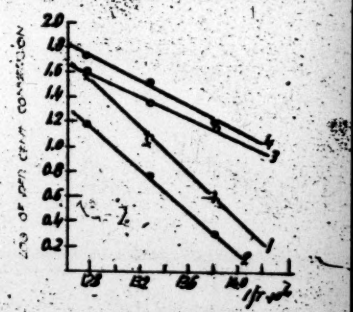


Fig. 12. Variation of the logarithm of per cent conversion into tics with temperature, at ω = = constant.

1 – Heptane; 2 – isooctane; 3 – 2-methylhexene-2; 4 – heptene-1

experiments, the ratio of the per cent conversion of heptane into unsaturated hydrocarbons to its per cent conversion into aromatic ones is practically constant at 0.7 within the contact time range of 1 to 7 seconds, dropping to 0.55 as the contact time is lengthened to 13 seconds (Fig. 11).

We plotted curves showing the variation of the logarithms of per cent conversion into aromatics, coke, and gas with 1/T for heptane, 2-methylhexene-2, and heptene, as well as for the overall per cent conversion (Figs. 12, 13, and 14), using the data tabulated in Tables 2 and 3. The corresponding values of the apparent activation energy and the temperature coefficients of the reaction rates are listed in Table 4. We found that the apparent activation energies of the reactions involved in the aromatization of heptane and isooctane are about twice as high as that of the overall conversion process, which is close to the apparent activation energy of the process involved in the formation of coke and gas. The absolute value of the apparent activation energy computed by us for the aromatization of heptane with a chrome catalyst is much lower

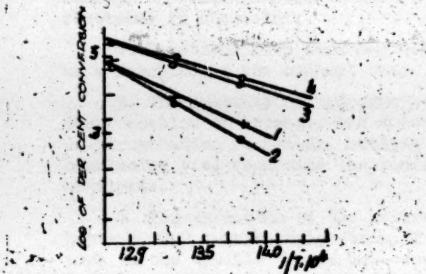


Fig. 13. Variation of the logarithm of per cent conversion into total gas and coke with temperature, at ω = constant.

1 – Heptane; 2 – isooctane; 3 – 2-methylhexene-2; 4 – heptene-1.

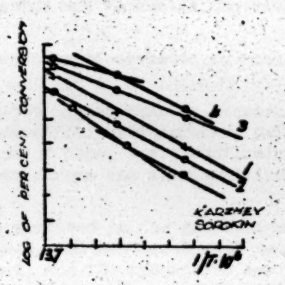


Fig. 14. Variation of the logarithm of overall per cent conversion with temperature, at ω = constant.

1 – Heptane; 2 – isooctane; 3 – 2-methylhexene-2; 4 – heptene-1.

than that calculated by Plate and Tarasova for its aromatization with a vanadium catalyst (50,700 cal/mole), though higher than the value computed by us from the experimental data of Karzhev and Sorokin (Fig. 1, Curve 1).

To compare our results with the data on the overall dehydrogenation reaction obtained by previous investigators, we have calculated the apparent activation energies of the overall dehydrogenation reaction (Table 4). The $E_{app.}$ = 39,800 cal/mole of heptane proved to be close to the figure secured by Plate and Tarasova of 41,000 cal/mole for the $E_{app.}$ of the overall dehydrogenation of n-heptane with a vanadium catalyst.

The $E_{app.}$ of the aromatization of the paraffin hydrocarbons heptane and isooctane are of the same order of magnitude, approx. 40,000 cal/mole, and about twice as high as the $E_{app.}$ of the aromatization of the olefin hydrocarbons: 2-methylhexene-2 and heptene-1. The comparatively low $E_{app.}$ for the reactions involved in the formation of coke and gas, approx. 20,000 cal/mole, in the aromatization of the paraffin hydrocarbons, and approx. 14,000 cal/mole for the

olefin hydrocarbons, is far out of line with the value found by Plate and Tarasova ($E_{app.}$ of coke formation = approx. 56,000 cal/mole in the aromatization of heptane with a vanadium catalyst). We ascribe the low values of $E_{app.}$ for the chrome catalyst to the fact that the formation of coke and gas are contact processes.

SUMMARY

1. Experiments have been run on the aromatization of n-heptane and 2-methylhexene-2 with a chrome catalyst at 480°.

The principal catalytic conversions of these hydrocarbons are the formation of aromatics, coke, and gas, the side reactions being the formation of unsaturated hydrocarbons in the aromatization of heptane and the formation of paraffins in the aromatization of 2-methylhexene-2.

2. Coke and gaseous hydrocarbons, aromatic and olefin hydrocarbons, and aromatic and paraffin hydrocarbons are formed simultaneously.

3. An induction period precedes the aromatization of heptane; the aromatization of 2-methylhexene-2 has no induction period and resembles the bimolecular reactions in character.

4. Equations have been derived for the formation of aromatic hydrocarbons as a function of the contact time.

5. The quantity of hydrogen evolved is 15-50% higher than is required for the formation of aromatic and unsaturated (or paraffin) hydrocarbons, owing to dehydrogenation reactions, causing the formation of coke, i.e., confirming our conclusion [14] regarding the similarity between chrome and aluminosilicate catalysts.

6. The variation of the several reactions involved in the conversion of heptane, 2,2,4-trimethylpentane, 2-methylhexene-2, and heptene-1 with temperature in the 450-510° range has been demonstrated, and the respective activation energies and temperature coefficients of the reaction rates have been calculated.

LITERATURE CITED

[1] A.F.Plate and G.A.Tarasova, J.Gen.Chem. 13, 21, 36 (1943).
[2] V.L.Karzhev and P.Z.Sorokin, J.Phys.Chem. 12, 48 (1938).
[3] B.L.Moldavsky and G.D.Kamusher, Coll. Wks. TsIATIM, vol. IV, p. 73, State Fuel Technology Press (1947).
[4] Pitkethly, Steiner, Trans. Faraday Soc., 35, 979, 1010 (1939).
[5] R.D.Obolentsev and Yu.N.Usov, J.Gen.Chem. 17, 897 (1947).
[6] Methods of Technical Analysis Applicable to the Synthesis of Hydrocarbon Fuels, State Scientific and Technical Press, p. 11-16. (1941)
[7] B.L.Moldavsky, G.Kamusher, and S.Livshits, J.Gen.Chem 7, 134 (1937).
[8] V.Moor, N.Strigaleva, and L.Shilaeva, J.Gen.Chem. 5, 819 (1935).
[9] S.R.Sergienko, Bull. USSR Acad. Sci., Div. Chem. Sci., 1941, 1, 177.
[10] B.P.Burlakov, Coll. Sci. Rep. by Students of Moscow State Univ., No. 22, Chemistry, p. 105 (1941).
[11] S.N.Obryadchikov. Selective Catalysis in Petroleum refining. State Fuel Technology Press, (1946).
[12] P.D.Obolentsev, Proc. USSR Acad. Sci., 66, No. 2 (1949).
[13] S.A.Kazeev. Kinetic Principles of Metallurgical Processes. Ministry of Defense Press. (1946).
[14] R.D.Obolontsev, "The Isomerizing Properties of Chromic Oxide," Symposium 6: Problems of Kinetics and Catalysis, p. 252. USSR Acad. Sci. Press (1949).
[15] G.N.Maslyansky and T.S.Berlin, J.Gen.Chem. 16, 1643 (1946).

Received June 15, 1948.

Chair of the Chemical Refining of Petroleum and Gas, The N.G.Chernyshevsky State University of Saratov

THE CONVERSION OF VINYL ETHERS

V. The Chemical Properties of Incomplete Acylals

of the $CH_3CH(OR)(OCOR_1)$ Type

N. F. Shostakovsky and N. A. Gershtein

In a preceding paper [1] we described a method of synthesizing incomplete acylals from vinyl ethers and carboxylic acids. The extraordinary simplicity of this method made these compounds available for laboratory and industrial use. Incomplete acylals have been known for a long time [2-4], but the only references to them in the literature deal with only one of their chemical properties: their hydrolyzability [5-7]. We reported earlier [8] that the mixed acetals $CH_3CH(OR)(OR_1)$ of analogous structure are readily disproportionated into the respective symmetric acetals; the incomplete acetals investigated in the present report did not display these properties under analogous conditions, though they possessed somewhat less stability. As a rule, distillation of acylals at atmospheric pressure in an atmosphere of oxygen results in their decomposition. The acylals secured from formic acid, $CH_3CH(OR)(OR)$, break down when distilled at normal pressure even in an atmosphere of nitrogen. Only when they are distilled in vacuum in a current of an inert gas are they secured in the chemically pure state and with high yields. Such simple representatives of the acylals as the acylals of acetic acid, $CH_3CH(OR)(OCOCH_3)$, can be distilled at normal pressure in an atmosphere of an inert gas, to be sure, but they undergo partial decomposition thereby, while the acylals recovered do not possess adequate chemical purity. Acylals are hydrolyzed by water in the cold, even when no catalyst is present, the rate of hydrolysis diminishing with the increase in size of the acid radical.

The addition of carboxylic acids to vinyl ethers takes place at various rates, depending upon the degree of dissociation of the acid. The addition of the first representative of the carboxylic acids, formic acid, to vinyl ethers produces a high exothermal effect, here again resembling the hydrohalic acids. The resultant acylals possess properties (ready decomposition, titrability with an alkali) that remind one of the α-halogenic ethers investigated in our laboratory by Shostakovsky and Bogdanova [9]

We were interested in ascertaining the ability of even the first representatives of the carboxylic acids (HCOOH, CH_3COOH), exhibiting a high degree of dissociation, to bring about the polymerization of the vinyl ethers. We proposed to attain our objective by running special tests under the conditions elaborated by Shostakovsky [10]: adding acid to the boiling vinyl ether. We found, however,

that under these conditions the carboxylic acids do not cause the vinyl ethers to polymerize. The reaction involved mainly the addition of the acid to the ether, resulting in the formation of incomplete acylals, though minute quantities of the corresponding acetals and esters:

$$CH_2{=}CH{-}O{-}R + R_1COOH \rightarrow \underset{\text{(I)}}{CH_3CH(OR)(OCOR_1)} + \underset{\text{(II)}}{CH_3CH(OR)_2} + \underset{\text{(III)}}{R_1COOR},$$

were detected in the reaction products.

Though the formation of the acetal (II) could be attributed to the disproportionation of the incomplete acylals, by analogy with the mixed acetals, the formation of the ester required further research.

We assume that the partial conversion of the acylal takes place as follows:

1 $CH_3CH(OR)(OCOR_1) \rightarrow CH_2{=}CH{-}OR + R_1COOH$ / $CH_2{=}CH{-}OCOR_1 + ROH$

2 $CH_2{=}CH{-}OR + ROH \longrightarrow CH_3CH(OR)_2$

3 $R_1COOH + ROH \rightarrow R_1COOR + H_2O$

4 $CH_2{=}CH{-}OCOR_1 + R_1COOH \longrightarrow CH_3CH(OCOR_1)_2$

5 $CH_3CH(OCOR_1)_2 + H_2O \longrightarrow CH_3CHO + 2R_1COOH$

The results of the interaction of vinyl n-butyl ether with acids (HCOOH, CH_3COOH) under polymerization conditions showed that the acylals (I) were the principal products of the reaction, their yields ranging from 61 to 84%. In addition to the by-products mentioned above – the acetals (II) and the esters (III) – we likewise found acetaldehyde and the respective acids, thus corroborating the set of reactions set forth above.

The present paper presents and discusses the results of experiments on the interaction of vinyl n-butyl and vinyl ethyl ethers with formic, acetic, and n-butyric acids, in which two new acylals were synthesized: ethoxyethylidene butyrate and butoxyethylidene butyrate:

$CH_3CH(OC_2H_5)(OCOC_3H_7)$, $CH_3CH(OC_4H_9)(OCOC_3H_7)$

One of the principal properties of acylals and acetals is their tendency to hydrolyze. Acylals hydrolyze extremely easily, when merely agitated with water, acetals being hydrolyzed by dilute mineral acids (2% H_2SO_4, etc.) in the cold. The resulting esters were saponified with alcoholic solutions of KOH. The hydrolysis reactions are as follows:

(I) $CH_3CH\begin{matrix}OR\\OCOR_1\end{matrix} + HOH \longrightarrow CH_3CHO + R_1COOH + ROH$

(II) $CH_3CH(OR)_2 + HOH \xrightarrow{H^+} CH_3CHO + 2ROH$

(III) $R_1COOR + KOH \longrightarrow R_1COOK + ROH$

The hydrolysis products were acetaldehyde, organic acids, and alcohols.

The methods of determination have been described in a previous paper [1], which also gives the computational formula.

The following methods were used to identify the structure and composition of the end products: 1) hydrolysis, followed by quantitative determination of the resulting acetaldehyde with sodium bisulfite; 2) hydrolysis, followed by quantitative determination of the resulting acid by titration with a 0.1 N solution of alkali; and 3) hydrolysis of the esters with alcoholic KOH.

EXPERIMENTAL

I. Reaction of vinyl n-butyl ether with formic acid. A. 50 g (0.5 mole) of vinyl n-butyl ether was placed in a three-necked flask, fitted with a mercury seal, a mechanical stirrer, a reflux condenser, and a thermometer reaching to the bottom of the flask. 23 g (0.5 mole) of freshly distilled formic acid was added a drop at a time, during the course of 1 hour 30 minutes to the boiling vinyl ether (94-95°). The temperature began to rise, reaching 103°. After all the acid had been added, the mixture was set aside to stand overnight. The resultant 71.7 g of substance was then fractionated in vacuum in a current of purified, anhydrous nitrogen. A trap with a coil condenser chilled to -14 to -18° was inserted in the system to collect any volatile products. The first fractionation yielded the following results: Fraction 1, b.p. 22-59° at 25 mm, 6.2 g (9.86%); Fraction 2, b.p. 61-67.5° at 25 mm, 50.1 g (68.63%); Fraction 3, b.p. 125-140° at 25 mm, 10.6 g (14.52%); residue in the flask (tar) 2.6 g (3.5%); collected in the trap, 0.85 g (1.16%). Total: 70.35 g (97.73%).

Processing of the reaction products: the contents of the trap were dissolved in water and placed in a 1000-ml measuring flask. The bisulfite method disclosed the presence of 0.806 g of acetaldehyde, equivalent to 1.83 g of the initial vinyl ether or 2.675 g of the sought-for acylal. The fraction with a b.p. of 22-59° was diluted with sulfuric ether and then treated several times with distilled water in a separatory funnel. The ether layer was dried with freshly calcined Na_2SO_4, after which it yielded 3 g of a substance ($HCOOC_4H_9$) with the following constants:

B.p. 106.5-107.3°; d_{28}^{28} 0.8975; d_4^{20} 0.8965; n_D^{20} 1.3912; MR_D 27.034; computed 26.944.
0.1193 g substance: 13.10 g benzene: Δt 0.4823°; 0.2082 g substance; 13.10 g benzene: Δt 0.8532°. Found: M 96.88, 95.56. $C_5H_{10}O_2$. Computed: M 102.
Hydrolysis with alcoholic KOH. 0.0923 g substance: 8.8 ml 0.1 N HCl (K = 1.016). Found %: ($HCOOC_4H_9$) 98.80.

These data identify the substance recovered from Fraction 1 as butyl formate, the yield being 5.88% in terms of the acid. The aqueous extracts secured by washing Fraction 1 yielded 0.568 g of acetaldehyde by the bisulfite method and 1.35 g of HCOOH by titration with 0.1 N alkali. Fraction 1 therefore consisted of butyl formate, acetaldehyde, and formic acid.

Fraction 2, with a b.p. of 61-67.5°, was dried with freshly calcined Na_2SO_4, after which nearly all of it distilled at 62-62.5° and 22 mm. The product was

butoxyethylidene formate, the constants of which were:

d_{20}^{20} 0.9340; d_4^{20} 0.9323; n_D^{20} 1.4020; MR_D 38.40; computed 37.823.

0.1208 g substance: 13.68 g C_6H_6: Δt 0.3145°; 0.2361 g substance: 13.68 g C_6H_6; Δt 0.626°. Found: M 144, 141.4. $C_7H_{14}O_3$. Computed: M 146.

Hydrolysis with determination of the percent of the acylal from the acid. 0.1770 g substance: 11.6 ml 0.1 N NaOH. 0.1578 g substance: 10.2 ml 0.1 N NaOH (K = 1.039). Found %: 99.42, 98.68.

Hydrolysis with determination of the percent of the acylal from the acetaldehyde. 0.147 g substance: 21.5 ml 0.1 N I_2. 0.159 g substance: 23.69 ml 0.1 N I_2 (K = 0.9075). Found %: 97.23, 98.60.

Fraction 3, with a b.p. of 125-140°, was diluted with absolute ether and then treated with metallic sodium to eliminate any free butyl alcohol or formic acid that might be present. Fractionation of the filtrate secured after removal of the resultant precipitate yielded 6.35 g of a substance with a m.p. of 184-185°, n_D^{20} 1.4090, corresponding to dibutyl acetal (which is described in full below), and 1.15 g of a substance with a b.p. of 192-195°, n_D^{20} 1.4250, which was not analyzed any further.

Our findings indicate that most of Fraction 3 consisted of dibutyl acetal.

B. This experiment was performed under the same conditions as the preceding one, merely the rate of addition of the acid being varied. The latter was added during the course of 5 minutes, the reagent quantities remaining the same: 0.5 mole of each ingredient.

Results of the first fractionation: Fraction 1, b.p. 25-32° at 23 mm, 9.3 g (12.74%); Fraction 2, b.p. 53-66° at 23 mm, 45.2 g (61.92%) (most distilling at 64-66°); Fraction 3, b.p. 31-49° at 4 mm, 9.0 g (12.33%); Fraction 4, b.p. 94-125° at 4 mm, 5.5 g (7.53%); residue in the flask (tar), 2.8 g (3.84%). Total: 71.8 g (98.36%).

The processing of the reaction products followed the same lines as before. Using the bisulfite method with the aqueous extracts of Fraction 1 yielded 1.385 g of acetaldehyde, while titration with 0.1 N NaOH yielded 3.47 g of formic acid. After the ether solution of Fraction 1 had been dried with freshly calcined Na_2SO_4, it yielded 3.6 g (7.06% in terms of the acid) of butyl formate, the constants of which were:

B.p. 105.8-106.2°; d_{20}^{20} 0.8918; d_4^{20} 0.8967; n_D^{20} 1.3912; MR_D 27.034; computed 26.944.

Refractionation of Fraction 2 yielded the principal reaction product: 44.5 g (60.96% of the theoretical) of butoxyethylidene formate, with the following constants:

B.p. 63.5-64.5° at 23 mm; d_{20}^{20} 0.9335; d_4^{20} 0.9318; n_D^{20} 1.4028; MR_D 38.22; computed 37.823.

0.1743 g substance; 15.05 g C_6H_6: Δt 0.4205°. 0.2785 g substance; 15.05 g C_6H_6: Δt 0.675°. Found: M 141.5, 140.7; $C_7H_{14}O_3$. Computed M 146.

Hydrolysis with determination of the per cent of the acylal from the acetaldehyde. 0.2268 g substance: 33.4 ml 0.1 N I_2; 0.1809 g substance: 27.2 ml 0.1 N I_2 (K = 0.9075). Found %: 97.56, 99.61.

Hydrolysis with determination of the per cent of the acylal from the acid. 0.1325 g substance: 8.6 ml 0.1 N NaOH; 0.1255 g substance: 8.2 ml 0.1 N NaOH (K = 1.039). Found %: 99.30, 98.80.

Fraction 3, with a b.p. of 31.5-49° at 4 mm, was treated with metallic sodium in an ether solution, yielding 5.6 g (6.44%, based on the vinyl ether) of a substance with a b.p. of 183.5-185°; n_D^{20} 1.4088. The product was combined with the analogous product of the first experiment and redistilled, yielding 9.6 g of a pure substance with the following constants:

B.p. 185-186°; d_{20}^{20} 0.8361; d_4^{20} 0.8346; n_D^{20} 1.4090; MR_D 51.33; computed 51.666.

0.2443 g substance; 15.08 g C_6H_6: Δ t 0.4955°. 0.4426 g substance; 15.08 g C_6H_6: Δ t 0.846°. Found: M 167.7, 171.9. $C_{10}H_{22}O_2$. Computed: M 174.

Hydrolysis with 2% sulfuric acid and determination of the per cent of the acylal from the acetaldehyde. 0.2085 g substance: 26.3 ml 0.1 N I_2; 0.1958 g substance: 24.6 ml 0.1 N I_2 (K = 0.9075). Found %: 99.57, 99.20.

These are the constants for dibutyl acetal. The results of both these experiments indicate that the rate at which the acid is added has no effect upon the course of the reaction.

II. Reaction of vinyl n-butyl ether with acetic acid. This experiment was carried out under the same conditions as above, the ingredients being added in the reverse order, however. 50 g (0.5 mole) of vinyl n-butyl ether was added drop by drop, in the course of 1½ hours, to 30 g (0.5 mole) of glacial acetic acid heated over a boiling water bath (temperature within the flask 98°). The temperature of the reaction mass rose to 101-102°, staying there as long as the ether was added. After all the vinyl n-butyl ether had been added, the reaction mass was heated for another 15 minutes over the boiling water bath and then set aside to stand for 18 hours. This yielded 78.1 g of a fragrant, slightly yellowish, transparent, and rather mobile liquid, fractionation of which yielded the following fractions (fractionation was carried out in a current of purified, anhydrous nitrogen): Fraction 1, b.p. 30-60° at 26 mm, n_D^{20} 1.4000, 7.9 g; Fraction 2, b.p. 60-73° at 26 mm (bulk at 72-73°), n_D^{20} 1.4035, 30.1 g; Fraction 3, b.p. 74-75° at 26 mm, n_D^{20} 1.4040, 25 g; Fraction 4, b.p. 75° at 26 mm, n_D^{20} 1.4040, 11.2 g; collected in trap, 3.8 g. Total: 78.0 g (97.5%).

The contents of the trap did not dissolve completely in water. The water soluble portion was placed in a 200 ml measuring flask and analyzed by the bisulfite and alkali methods. The bisulfite method yielded 0.1297 g of acetaldehyde, while titration with alkali yielded 1.945 g of acetic acid. The water-insoluble portion, totaling 1 g, was desiccated with calcined potash and proved to be vinyl n-butyl ether, with a b.p. of 92.8-93.4°; n_D^{20} 1.4016. The figures in the literature for vinyl n-butyl ether are: b.p. 93.3°; n_D^{20} 1.4015 [11].

The resulting fractions were then processed as follows. As the results of the first fractionation indicated, all the fractions but the first had adjacent boiling points and refractive indexes, so that Fraction 1 was processed separately.

After treatment with fused potash to bind the free acetic acid and drying, the filtrate of Fraction 1 was refractionated, the following two fractions being collected: Fraction 1, b.p. 123-127°, n_D^{20} 1.3955, 1.5 g; Fraction 2, b.p. 168-169.6°, n_D^{20} 1.4040, 3.5 g; the residue left in the flask totaled 2.8 g.

The fractionation results indicate that the bulk of Fraction 1 also consisted of an acylal - butoxyethylidene acetate.

The fraction with a b.p. of 123-127° was redistilled, yielding 1 g of a substance the constants of which identified it as butyl acetate.

B.p. 124-126°; d_{20}^{20} 0.8823; d_4^{20} 0.8807; n_D^{20} 1.3950; MR_D 31.57; computed 31.562.

Hydrolysis with alcoholic KOH. 0.1534 g substance: 12.85 ml 0.1 N HCl (K = 1.016); 0.1822 g substance: 15.5 ml 0.1 N HCl (K = 1.016). Found %: $CH_3COOC_4H_9$. 98.72, 100.3.

Fraction 1 (b.p. 30-60° at 26 mm) thus contained a negligible quantity of butyl acetate (about 1.5 g), most of it consisting of butoxyethylidene acetate, which was combined with the bulk of the product for purification. Further vacuum fractionations of the reaction products in a current of purified anhydrous nitrogen yielded 68 g (85% of the calculated theoretical quantity) of a pure substance with the following constants:

B.p. 42.5-43° at 3 mm: d_{28}^{28} 0.9210; d_4^{20} 0.9193; n_D^{20} 1.4040; MR_D 42.55; computed 42.441.

0.1932 g substance; 14.58 g C_6H_6: Δt 0.416°. 0.2947 g substance; 14.58 g C_6H_6: Δt 0.640°. Found: M 163.3, 162. $C_8H_{16}O_3$. Computed: M 160.

Hydrolysis with determination of the per cent of acylal from the acetaldehyde. 0.2491 g substance: 33.5 ml 0.1 N I_2; 0.2493 g substance: 33.9 ml 0.1 N I_2 (K = 0.9075). Found %: 97.64, 98.73.

Hydrolysis with determination of the per cent of acylal from the acid. 0.2553 g substance: 15.7 ml 0.1 N NaOH. 0.2528 g substance: 15.65 ml 0.1 N NaOH (K = 1.039). Found %: 102.2, 102.9.

We had observed excessively high results in alkali titration earlier [1], but we have not found out why this occurs. It is not impossible that traces of the complete acylal are present, as a result of the reaction. It was impossible to isolate it, inasmuch as the two boiling points are almost identical, ranging, according to the literature, from 116.8 to 169° [2].

Lastly, the flask residue (of about 2 g) was dissolved in absolute ether and treated with metallic sodium, yielding 0.6 g of a pure substance with a b.p. of 184-185°; n_D^{20} 1.4088.

Hydrolysis with 2% sulfuric acid and determination of the percent of acylyl from the acetaldehyde. 0.1046 g substance: 11.85 ml 0.1 N I_2. 0.0995 g substance: 11.35 ml 0.1 N I_2 (K = 0.9899). Found %: 97.57, 98.24.

These findings show that it was identical with dibutyl acetate.

This test indicates that the order in which the ingredients are added likewise has no effect upon the course of the reaction.

III. Synthesis of the ethoxyethylidene butyrate. The initial substances were: vinyl ethyl ether with a b.p. of 35.9-36.2° at 758 mm; n_D^{20} 1.3775; and normal butyric acid, with a b.p. of 161°; n_D^{20} 1.4005.

A mixture of 36 g (0.5 mole) of vinyl ethyl ether and 44 g (0.5 mole) of butyric acid was heated in a sealed ampoule for 15 hours over a boiling water bath. Double vacuum fractionation in a current of purified anhydrous nitrogen yielded 75.2 g of the pure product (94% of the theoretical), with the following constants:

B.p. 81-81.5° at 28 mm, 37.5-38 at 4.5 mm; d_{28}^{28} 0.9237; d_4^{20} 0.9221; n_D^{20} 1.4030; MR_D 42.33; computed 42.441.

0.2014 g substance; 13.46 g C_6H_6: Δt 0.490°; 0.1246 g substance; 13.21 g C_6H_6: Δt 0.3042°. Found: M 156.7, 159.7. $C_8H_{16}O_3$. Computed M 160.

12.52 mg substance: 27.35 mg CO_2; 11.65 mg H_2O. 12.28 mg substance: 26.75 mg CO_2; 11.31 mg H_2O. Found %: C 59.61, 59.47; H 10.41, 10.30. $C_8H_{16}O_3$. Computed %: C 60; H 10.

Hydrolysis by 2% sulfuric acid with determination of the per cent of acylal from the acetaldehyde. 0.1068 g substance: 12.59 ml 0.1 N I_2. 0.1328 g substance: 15.95 ml 0.1 N I_2 (K = 1.009). Found %: 97.88, 96.95.

Hydrolysis with determination of the per cent of acylal from the acid. 0.0513 g substance: 10.3 ml 0.1 N NaOH; 0.1781 g substance: 12.25 ml 0.1 N NaOH. (K = 0.909). Found %: 98.36, 100.

IV. Synthesis of butoxyethylidene butyrate. The initial substances were: vinyl n-butyl ether, with a b.p. of 93.5-94°; n_D^{20} 1.4020; and normal butyric acid, with a b.p. of 161°; n_D^{20} 1.4005.

A mixture of 25 g (0.25 mole) of vinyl n-butyl ether and 22 g (0.25 mole) of normal butyric acid was heated in a sealed ampoule for 15 hours over a boiling water bath. Double fractionation yielded 44.2 g (94.04% of the theoretical) of a wholly pure substance with the following constants:

B.p. 74.5-75.2° at 7 mm, 59-59.1° at 2.5 mm; d_{20}^{20} 0.9032; d_4^{20} 0.9016. n_D^{20} 1.4118; MR_D 51.78; computed 51.677.

0.1166 g substance; 12.45 g C_6H_6: Δt 0.269°. 0.2224 g substance; 12.45 g C_6H_6: Δt 0.5025°. Found M 178.5, 182.3. $C_{10}H_{20}O_3$. Computed M 188.

2.690 mg substance: 6.330 mg CO_2; 2.560 mg H_2O; 3.385 mg substance: 7.968 mg CO_2; 3.229 mg H_2O. Found %: C 64.22, 64.19; H 10.65, 10.67. $C_{10}H_{20}O_3$. Computed %: C 63.83; H 10.64.

Hydrolysis with determination of the per cent of acylal from the acetaldehyde. 0.0998 g substance: 10.3 ml 0.1 N I_2; 0.0609 g substance: 6.4 ml 0.1 N I_2 (K = 1.009). Found %: 97.89, 99.67.

Hydrolysis with determination of the per cent of acylal from the acid. 0.166 g substance: 9.8 ml 0.1 N NaOH; 0.208 g substance: 12.2 ml 0.1 N NaOH (K = 0.909). Found %: 100.3, 100.2.

SUMMARY

1. A study has been made of the reaction of vinyl ethers with carboxylic acids under conditions where the former are polymerized, by adding the acid to the boiling vinyl ether. It has been shown that carboxylic acids, even their lowest representatives, which possess a rather high degree of dissociation, do not bring about polymerization of vinyl ethers. The main course of the reaction is the addition of the carboxylic acids to the vinyl ethers, yielding incomplete acylals.

2. It has also been found that low yields (3-5%) of the corresponding symmetric acetals (II) and esters (III) are secured.

3. The results have been discussed, and a mechanism suggested for the reaction involved in the formation of the products (II) and (III) as the result of transformation of the incomplete acylals.

LITERATURE CITED

[1] N.A.Gershtein and M.F Shostakovsky, J.Gen. Chem. 18, 1989 (1948).
[2] Geuther, Ann., 106, 249 (1858); 225, 265 (1884).
[3] Gutrie u. Kolbe, Ann., 109, 298 (1859). Schijt, 9, 304 (1876).
[4] E.Wedekind, Ber., 36, 1383 (1903).
[5] A.Skrabal, Z. phys.chem., 111, 120 (1924).
[6] R.Leutner, M., 60, 342 (1932); 66, 222 (1935).
[7] Palomaa and co-workers, Ber., 66, 468 (1933).
[8] M.F.Shostakovsky, N.A.Gershtein, J.Gen.Chem. 16, 937 (1946); 18,451 (1948).
[9] M.F.Shostakovsky and A.V.Bogdanova, J.Gen.Chem. 17, 565 (1947).
[10] M.F.Shostakovsky, J.Gen.Chem. 13, 674 (1943); 14, 102 (1944).
[11] A.E.Favorsky, M.F.Shostakovsky, J.Gen.Chem. 13, 1 (1943).

Received October 27, 1949. Vinyl Compounds Lab., Inst. Organic Chemistry, USSR Academy of Sciences

THE REACTION OF DIMETHYLETHYNYLCARBINOL WITH PROPYLENE OXIDE . II

K. D. Petrov and E. S. Lagucheva

We have shown [1] that dimethylethynylcarbinol reacts with ethylene oxide in the presence of tertiary organic bases to form the β-hydroxy ethyl ether of dimethylethynylcarbinol. We wanted to find out how dimethylethynylcarbinol would react with the closest homolog of ethylene oxide, propylene oxide.

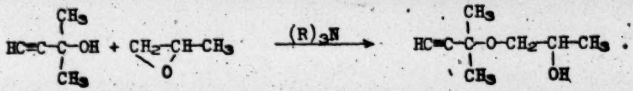
We condensed dimethylethynylcarbinol with propylene oxide in the presence of dimethylaniline and methyldiethanolamine. We used dimethylethynylcarbinol and propylene oxide in 3:1 molar proportions, while the catalyst totaled 4% of the carbinol. When dimethylaniline was employed, the yield of the monoether was 74.4%, based on the reacted carbinol, while the yield was only 32.6% when methyldiethanolamine was used.

The monoether distilled at normal pressure without any signs of decomposition and it was alkali-resistant and insoluble in water, which is probably why it did not display the qualitative reaction with ammoniacal silver nitrate. The presence of a triple bond was proved by its reaction with a 2% aqueous solution of corrosive sublimate, yielding a curdy, white precipitate, and by its decolorizing an aqueous solution of potassium permanganate and a chloroform solution of bromine. The molecular weight, molar refraction, and number of hydroxyl groups found for the monoether all agreed with the values calculated theoretically.

The one problem left to decide was the sequence in which the dimethylethynylcarbinol was added to the propylene oxide.

Owing to the asymmetrical nature of propylene oxide, alcohols can be added to it in two ways, yielding primary or secondary monoethers, the order of adding the alcohols to asymmetrical oxides depending upon the nature of the catalyst [2,3,4]. The effect of the nature of the catalyst upon the order in which alcohols are added to asymmetrical oxides was first discovered by Petrov and Tyazhelova in their research on the reaction of alcohols with isobutylene oxide. They later made a study of the order in which alcohols are added to propylene oxide. Their observations indicate that the condensation of propylene oxide with alcohols in the presence of acid catalysts yields a mixture of primary and secondary ethers, whereas the use of alkaline catalysts yields primary ethers [2,5]. This rule was subsequently confirmed by the researches of Chitwood and Freure [3].

In the light of the foregoing, it may be asserted that here again the condensation of dimethylethynylcarbinol with propylene oxide in the presence of tertiary organic bases will give rise to a primary monoether:



Moreover, the fact that the boiling point of this ether of dimethylethynylcarbinol (167.5-169°) is lower than that of the β-hydroxy ethyl ether (170.5-172°) supports this structure of the ether. The acetate of the β-hydroxy propyl ether of dimethylethynylcarbinol, prepared by reacting the latter with acetic anhydride, likewise has a lower boiling point than the acetate of the β-hydroxy ethyl ether of dimethylethynylcarbinol.

EXPERIMENTAL

Synthesis of the β-hydroxy propyl ether of dimethylethynylcarbinol in the presence of dimethylaniline. In the synthesis of the β-hydroxypropyl ether of dimethylethynyl carbinol we used a dimethylethynylcarbinol prepared as specified by Favorsky [8], with a b.p. of 101-104°; d_{20}^{20} 0.868; n_D^{20} 1.4220; and a propylene oxide with a b.p. of 35°; d_{20}^{20} 0.859.

The β-hydroxy propyl ether of dimethylethynylcarbinol was synthesized under the following conditions: 199.7 g (2.38 mole) of dimethylethynylcarbinol, 46.9 g (0.81 mole) of propylene oxide, and 9 g of dimethylaniline were charged into an autoclave fitted with a stirrer and a thermocouple. Then the autoclave was heated until its temperature reached 145-155°, the process being carried out at this temperature for 8 hours with constant stirring. When this time was over, the autoclave was cooled, and the reaction product was removed and sent off for fractionation.

Fractionation was carried out in a flask fitted with a herringbone dephlegmator one meter high. At the start, the unreacted propylene oxide, totaling 20 g and the initial dimethylethynylcarbinol, totaling 177 g, were driven off at standard pressure. Then fractionation was pursued in vacuum. Vacuum fractionation yielded the following fractions: Fraction 1, up to 58° (5.5 mm) – 10 g; n_D^{20} 1.4250; Fraction 2, 58-60° (5.5 mm)– 16 g; n_D^{20} 1.4407; still residue – 12 g.

The fraction with a boiling point of 58-60° (5.5 mm) was the β-hydroxy propyl ether of dimethylethynylcarbinol, with a yield of 74.4% of the theoretical, based on the reacted dimethylethynylcarbinol. The β-hydroxy propyl ether of dimethylethynylcarbinol is a faintly greenish, transparent liquid. It is insoluble in water or alkalies, but is freely soluble in organic solvents; it decolorizes a solution of bromine in chloroform and an aqueous solution of potassium permanganate; and it forms a curdy, white precipitate when shaken with a 2% aqueous solution of corrosive sublimate. It distils at 167.5-169° at standard pressure without any signs of decomposition.

d_{20}^{20} 0.9282; n_D^{20} 1.4407; MR_D 40.30; computed 40.31.

0.2279 g substance: 38.2 ml 0.5 N KOH; 0.2374 g substance; 38.1 ml 0.5 N KOH. Control test: 42.25 ml 0.5 N KOH (K = 0.822); 0.7800 g substance; 26.68 g benzene: Δt 1.03°. Found %: OH 12,30, 12.20 (phthalonation method). M 145.4. $C_8H_{14}O_2$. Computed %: OH 12.00; M 142.

Acetate of the β-hydroxy propyl ether of dimethylethynylcarbinol. 17.75 g (0.125 mole) of the β-hydroxy propyl ether of dimethylethynylcarbinol and 38 g (0.375 mole) of acetic anhydride were heated together for 3 hours with constant stirring in a flask fitted with a reflux condenser. Then 10 ml of water was added to decompose the excess anhydride, and heating was continued for another 30 minutes. The reaction mixture was then cooled and neutralized, while being stirred, with a saturated solution of soda. The ether layer was separated from the aqueous one, three ether extracts being made of the latter and then combined

with the bulk of the product. The product was then desiccated with sodium sulfate and filtered. The sulfuric ether was driven off over a water bath, and the reaction product was fractionated in vacuum, yielding: Fraction 1, up to 84.5° (17.5 mm), 1.5 g; Fraction 2, 84.5-86.5° (17.5 mm), 21 g; residue 1.3 g.

The yield of the acetate of the β-hydroxy propyl ether of dimethylethynylcarbinol, distilled at 84.5-86.5° (17.5 mm) was 91% of the theoretical. The product was neutral.

d_4^{20} 0.9619; n_D^{20} 1.4250; MR_D 49.00; computed 49.67.

0.4230 g substance: 16.92 ml 0.5 N HCl; 0.4352 g substance: 16.55 ml 0.5 N HCl. Control test: 21.85 ml 0.5 N HCl (K = 0.953). Found: ester number 310.5, 308.3. $C_{10}H_{16}O_3$. Computed ester number 304.2.

SUMMARY

1. It has been shown that dimethylethynylcarbinol reacts with propylene oxide in the presence of tertiary organic bases, yielding the β-hydroxypropyl ether of dimethylethynylcarbinol, which has not been described in the literature. The reaction is similar to that with ethylene oxide.

2. The acetoxy propyl ether of dimethylethynylcarbinol is described and its properties given.

LITERATURE CITED

[1] K.D.Petrov and E.S.Lagucheva, J.Gen.Chem. 21, 1247 (1951); K.D.Petrov and E.S.Lagucheva, Certificate of Authorship No. 76,370.

[2] A.A.Petrov, J.Gen.Chem. 14, 1038 (1944).

[3] H.C.Chitwood and B.T.Freure, J.Am.Chem.Soc., 68, 680 (1946).

[4] A.A.Petrov, J.Gen.Chem. 16, 1625 (1946).

[5] A.A.Petrov, J.Gen.Chem. 16, 1206 (1946).

[6] A.E.Favorsky, Certificate of Authorship No. 31017.

Received August 20, 1949.

The M.V.Frunze Plastics Research Institute

ACETYLENE – ALLENE REARRANGEMENTS

II. The Reaction of Alcoholic Alkali and of Alcoholates and Acetates of the Alkali Metals upon Acetylene and Allene Chlorides

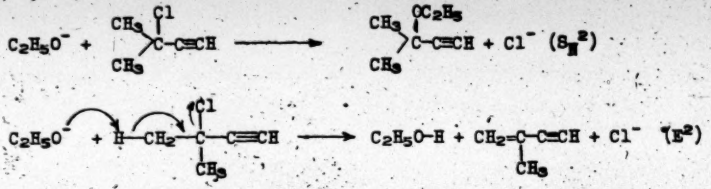
A. N. Pudovik

The action of an alcoholic alkali and of alcoholates of the alkali metals upon allyl halide isomers has been investigated in detail by the present author and described in several papers [1]. It was found that alkalies act differently upon allyl halide isomers in solutions of primary, secondary, and tertiary alcohols, and the importance of the reagent concentration for the mechanism of the reactions was likewise pointed out.

Continuing our work along these lines, we were greatly interested in exploring the reactions of an alcoholic alkali and alcoholates of the alkali metals with acetylene and allene chlorides. Absolutely no work can be found in the literature on this topic at the present time. In one of I.N.Nazarov's papers [2], the author notes that the action of an alcoholic alkali upon dimethylvinyl ethynylchloromethane splits off hydrogen chloride and yields nothing but an unsaturated hydrocarbon. He recommends that dimethylvinylethynylcarbinol be reacted with alcohols in the presence of sulfuric acid to secure ethers of the carbinol. There is no other information in the literature on the subject. As will be seen from what follows, I.N.Nazarov's assertion has no foundation in fact. The reactions of acetylene chlorides with alkalies and with alcoholates of the alkali metals in alcohol solution result in the formation of the corresponding ethers of the alcohols used in the reactions, in addition to unsaturated hydrocarbons. The proportions of the products formed depend largely upon the proportions of the reagents used in the reaction and upon how the latter is carried out. A study of these reactions is of definite theoretical interest in several respects: the effect of changing the reaction conditions upon the proportions of the substitution and cleavage reactions; the influence of the nature of the alcohols upon the course of the reaction; and the mechanism of the possible acetylene-allene rearrangements during monomolecular alcoholysis. In the first series of tests we investigated the action of caustic potash and of alcoholates of the alkali metals in concentrated alcoholic solution upon dimethylethynyl chloromethane and 1-chloro-3-methylbutadiene-1,2. According to the Hughes, Ingold, Mastermann, and Nulty [3] investigation of the kinetics of alcoholysis of tert-butyl chloride, the transition point from the monomolecular to the bimolecular reaction is at a 0.1 N solution of the alcoholic alkali, the reaction being monomolecular below this concentration and bimolecular above it. In the critical concentration region (near 0.1 N) the reactions are both monomolecular and bimolecular.

Inasmuch as we carried out the experiments mentioned above in solutions whose concentrations were about 3 N with respect to the alkali and the alcoholates, it is evident that the substitution and cleavage reactions taking place under these conditions must be bimolecular on the whole.

The reaction of dimethylethynylchloromethane with caustic potash and with sodium alcoholate in alcohol yielded isopropenylacetylene and the ethyl ether of dimethylethynylcarbinol, the yield of the ether being 57% of the mixture in the first case and 51% in the second. The total yield of the hydrocarbon and the ether ranged from 66 to 70% in different tests. The ether displayed the characteristic qualitative reaction for acetylenic hydrogen with ammoniacal silver nitrate. Both reactions: the substitution and the cleavage, take place independently, in the same stage, as was to be expected in view of their assumed bimolecular nature, and may be represented by the following equations:



When dimethylethynylchloromethane was reacted with caustic potash and sodium alcoholate in methanol, the yield of isopropenylacetylene was much lower, the principal reaction product being the methyl ether of dimethylethynylcarbinol in each case. The structure of the synthesized ethers was proved by synthesizing them in a different manner: by reacting methanol and ethyl alcohol with dimethylethynylcarbinol in the presence of a small quantity of concentrated sulfuric acid. The resultant ethers had the same constants as those secured by the first method from dimethylethynylchloromethane, though their yields were extremely minute.

The reaction of dimethylethynylchloromethane with sodium phenolate enabled us to secure a slight yield of nothing but the phenyl ether of dimethylethynylcarbinol.

We then investigated the action of sodium alcoholate upon the allene chloride 1-chloro-3-methylbutadiene-1,2 dissolved in methanol. The yield of the allene ether 1-methoxy-3-methylbutadiene-1,2 did not exceed 15% of the theoretical, notwithstanding a series of experiments run under different conditions. In addition to the allene ether, we secured high boiling products, which were not fractionated. The allene ether is a liquid with an acrid odor, which did not yield a precipitate when ammoniacal silver nitrate was added to it.

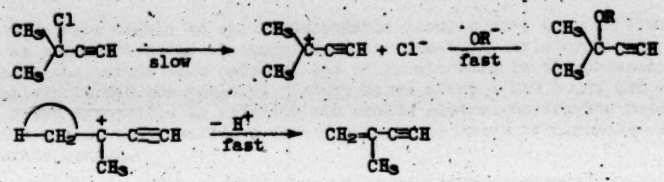
The ether was saponified by shaking it up with a 5% solution of sulfuric acid. Adding p-dinitrophenylhydrazine and semicarbazide to the resulting solution yielded the p-dinitrophenylhydrazone and the semicarbazide, respectively, of β,β-dimethylacrolein, the melting points of which were 175-176° and 219-220°, respectively, after recrystallization. We were unable to secure the allene ether in the pure state when the reaction was carried out by reacting the allene chloride, 1-chloro-3-methylbutadiene-1,2 with the alcoholate in ethyl alcohol.

We also investigated the reaction of dimethylethynylchloromethane with methanol and ethyl alcohol in a neutral medium.

In both tests the principal reaction products were the respective ethers of dimethylethynylcarbinol, with only a minute quantity of isopropenylacetylene; no

isomeric esters of the allene type were found.

The formation of ethers and of an unsaturated hydrocarbon in this case must be largely monomolecular and may be represented by the following equations:



In contrast to the bimolecular reaction that takes place in a single stage, the monomolecular reaction takes place in two stages. In the first stage, the solvent dissociates the acetylenic halogen derivative into a halogen ion and a positively charged carbonium ion. In the second stage, the carbonium ion adds an alkoxy ion, forming an ether liberating a proton, and forming isopropenylacetylene. Inasmuch as the dissociation of the acetylenic halogen derivative takes place much more slowly in the first stage than the reaction occurring in the second stage, it is this dissociation that governs the rate of the entire transformation. The process is monomolecular and is represented by a first-order reaction. The conditions under which the reaction is carried out do not preclude, however, a partial bimolecular reaction between the acetylenic halogen derivative and molecules of the solvent, which is again a first-order reaction. Analogous experiments carried out with primary and secondary allyl halogen compounds indicate, however, that bimolecular reactions with the solvent are negligible, especially in the case of the secondary isomers, the principal reaction being monomolecular. This bimolecular reaction with the solvent will be even more insignificant in the case of tertiary acetylenic chlorides, obviously, as they have an even greater tendency to monomolecular reactions than do the secondary allyl halide isomers.

Comparison of the results of our experiments on dimethylethynylchloromethane demonstrates that much more hydrogen chloride is evolved during the bimolecular alcoholysis of that compound dissolved in ethyl alcohol than in monomolecular alcoholysis in the same alcohol. This conclusion conforms to the results secured in analogous reactions with secondary and tertiary alkyl halides [3]. The lower percentage of an unsaturated hydrocarbon formed from dimethylethynylchloromethane in a bimolecular reaction than is the case with tert-butyl chloride is apparently due to the difference in the structure of the radicals of these two compounds. We know that the ratio of the reaction rates for cleavage and substitution in the bimolecular reaction diminishes gradually as we pass from tertiary alkyl halides to the secondary and primary ones.

Results of the same sort were secured in our investigation of the action of alcoholic alkali and alcoholates of the alkali metals upon dimethylvinylethynylchloromethane. Reacting the chloride with caustic potash and alcoholates in a concentrated solution of methanol, i.e., under conditions favoring bimolecular alcoholysis, yielded a mixture of isopropenylvinylacetylene and the methyl ether of dimethylvinylethynylcarbinol.

We were unable to secure dependable results when the reaction was carried out as a monomolecular alcoholysis of the dimethylvinylethynylchloromethane, as heating the latter with methanol and ethyl alcohols in the presence of phenolphthalein turned the reaction mixture brown after a few hours had elapsed; it was found impossible to maintain the medium neutral during the reaction by means of titration, while making a periodic check by means of checking samples was not accurate enough.

Reacting sodium and potassium acetates with dimethylvinylethynylchloromethane in a solution of glacial acetic acid yielded isopropenylvinylacetylene and dimethylvinylethynylcarbinol acetate. The reaction products contained no acetate of allene structure.

Saponification of the dimethylvinylethynylchloromethane in a neutral aqueous solution, i.e., in monomolecular hydrolysis, yielded dimethylvinylethynylcarbinol as the sole reaction product.

The results secured in the present research may be of great importance in the study of the mechanism involved in acetylene-allene rearrangements.

EXPERIMENTAL

Dimethylethynylchloromethane was prepared by the well-known T.A.Favorskaya method [4], involving the reaction of dimethylethynylcarbinol with hydrochloric acid in the presence of cuprous chloride and ammonium chloride. One disadvantage of this method is the circumstance that the formation of this chloride is paralleled by the formation of a large quantity of the isomeric allene chloride, together with dichlorides and a large amount of tar. In order to work out a method for the preparation of dimethylethynylchloromethane as the chief end product, we ran tests involving the reaction of dimethylethynylcarbinol with the following: a) anhydrous hydrogen chloride; b) concentrated hydrochloric acid; and c) thionyl chloride.

a) 100 g of dimethylethynylcarbinol, prepared by the A.E.Favorsky method [5] - passing acetylene through an ether solution of acetone containing pulverized caustic potash - was saturated with anhydrous hydrogen chloride until its gain in weight totaled 43 g. The flask was then closed with a stopper attached to a calcium-chloride tube and set aside to stand at room temperature. The reaction was extremely slow. After standing for twenty-four hours, the mixture was diluted with water; the chloride layer was extremely small after it had been thoroughly washed with water. The reaction mixture was allowed to stand for a week, after which it was treated with water, the upper layer being removed, desiccated with calcium chloride, and distilled from a small flask into a Widmer column, yielding 16 g of dimethylethynylchloromethane, with a b.p. of 73-76°; n_D^{20} 1.4200.

b) 20 g of dimethylethynylcarbinol was heated with 50 g of concentrated hydrochloric acid for 8 hours in a sealed tube over a water bath. Then the mixture was diluted with water and extracted with ether. The ether extract was desiccated with calcium chloride, the ether was driven off, and the residue was fractionated. This yielded 4 g of dimethylethynylchloromethane and a small quantity of high-boiling fractions.

c) 17 g of thionyl chloride was gradually added from a dropping funnel to 20 g of dimethylethynylcarbinol chilled with a freezing mixture. After the reaction mixture had stood for an hour, it was diluted with water and extracted

with ether. Fractionation of the ether extract yielded 3.2 g of dimethylethynylchloromethane, with a b.p. of 74-76°, plus several high-boiling fractions.

We have therefore established that dimethylethynylchloromethane is produced by the action of hydrogen chloride upon dimethylethynylcarbinol, but that the yield is low. Nor do the other methods tested give high yields of the chloride. The method evolved by T.A.Favorskaya is still the best.*

Action of KOH on dimethylethynylchloromethane in ethyl alcohol. 17 g of caustic potash was dissolved in 80 g of ethyl alcohol, and 25 g of the chloride was added to the resulting solution. The reaction mass was heated for 4 hours with a reflux condenser over a water bath, after which the alcohol was driven off and diluted with water.

The layer that separated out was again treated with water, desiccated with calcium chloride, and fractionated from a small flask into a spiral Widmer column. This yielded 6.1 g of isopropenylacetylene, with a b.p. of 32-33°; n_D^{20} 1.4090, and 8.3 g of the ethyl ether of dimethylethynylcarbinol. The ether was a colorless liquid with a rather strong ether odor:

B.p. 93°; n_D^{20} 1.4042; d_4^{20} 0.8125; MR_D 33.71, computed 34.16.

0.0840 g substance: 0.2302 g CO_2; 0.0824 g H_2O. Found %: C 74.74; H 10.89. $C_7H_{12}O$. Computed %: C 75.00; H 10.71.

When a few drops of the ether were added to ammoniacal silver nitrate, a copious white precipitate was thrown down.

Action of sodium ethylate on dimethylethynylchloromethane in ethyl alcohol. 8 g of sodium was dissolved in 100 g of absolute ethyl alcohol, and 30 g of dimethylethynylchloromethane was added to the resultant solution. The reaction mass was then heated for 3 hours over a water bath, after which the alcohol was driven off and diluted with water.

The upper layer was retreated with water, desiccated with calcium chloride, and fractionated into a Widmer column. This yielded 7.6 g of isopropenylacetylene, with a b.p. of 33-35°; n_D^{20} 1.4090, and 8 g of the ethyl ether of dimethylethynylcarbinol, with a b.p. of 92-93°; n_D^{20} 1.4050.

Action of KOH on dimethylethynylchloromethane in methanol. 10 g of caustic potash was dissolved by heating it in 60 ml of anhydrous methanol, and the solution was transferred to a glass tube. 15 g of the chloride was added, and the tube was sealed and heated to 70-80° for 6 hours over a water bath. Then the reaction mixture was transferred to a flask connected to a Widmer dephlegmator to drive off the isopropenylacetylene. This yielded 1.1 g of isopropenylacetylene with a b.p. of 33-35°. The residue was treated with water, the resulting upper layer being desiccated with calcium chloride and fractionated, yielding 8.9 g of the methyl ether of dimethylethynylcarbinol.

B.p. 81°; n_D^{20} 1.4015; d_4^{20} 0.8135; MR_D 29.30, computed 29.54.

0.0878 g substance: 0.2350 g CO_2; 0.0836 g H_2O. Found %: C 72.99; H 10.58. $C_8H_{10}O$. Computed %: C 73.46; H 10.20.

---

* In 1949 there appeared a paper by Hurd and McPee [6], in which they assert that the reaction of dimethylethynylcarbinol with hydrochloric acid yields 2 methyl-3-chlorobutadiene-1,3, which is in complete contradiction with the results of my investigations of this reaction. In 1950 Hennon, Heegham, and Maloney [7] refuted the findings of Hurd and McPee as being unfounded in fact and came to the same conclusions as I had considerably earlier, i.e., that the reaction of dimethylethynylcarbinol with hydrochloric acid yields dimethylethynylchloromethane as the principal reaction product.

Action of sodium methylate on dimethylethynylchloromethane in methanol. 20 g of the chloride was added to the methylate, prepared from 5 g of sodium and 85 g of methanol. The reaction mass was then heated with a reflux condenser for 2 hours over a water bath. Further processing of the mixture yielded about 2 g of isopropenylacetylene and 10 g of the methyl ether of dimethylethynylcarbinol, with a b.p. of 80-82°; n_D^{20} 1.4020.

Action of potassium phenolate on dimethylethynylchloromethane. A solution of 15 g of KOH in 15 g of water was gradually added, with constant stirring, to 20 g of fused phenol, after which the reaction mass was cooled with water while 15 g of dimethylethynylchloromethane was added drop by drop. The reaction mass was then heated for 3 hours over a water bath, after which it was diluted with water and extracted with ether. The ether extract was desiccated with calcium chloride, the ether was driven off, and the residue was fractionated in vacuum, yielding five fractions that distilled in the 80-220° range at 10 mm. The first three fractions, which distilled at 80-105° and 10 mm, were again treated with an aqueous alkali solution. Refractionation of these fractions yielded the phenyl ether of dimethylethynylcarbinol, with a b.p. of 82-83° at 11 mm:

n_D^{20} 1.5150; d_4^{20} 0.9838; MR_D 49.15; computed 49.04.

0.1244 g substance: 0.3780 g CO_2; 0.0900 g H_2O. Found %: C 82.11; H 8.03. $C_{11}H_{12}O$. Computed %: C 82.50; H 7.5.

Synthesis of the methyl ether of dimethylethynylcarbinol from the carbinol and methanol. A mixture of 20 g of dimethylethynylcarbinol, 12 g of methanol, and 1.5 ml of concentrated sulfuric acid was heated for 6 hours over a water bath. Then the reaction mass was diluted with water, and the top layer was desiccated with calcium chloride and distilled, yielding 3.3 g of the methyl ether of dimethylethynylcarbinol, with a b.p. of 81-82°; n_D^{20} 1.4025; d_4^{20} 0.8140.

Synthesis of the ethyl ether of dimethylethynylcarbinol from the carbinol and ethyl alcohol. 15 g of dimethylethynylcarbinol, 10 g of ethyl alcohol, and 2 ml of concentrated sulfuric acid were heated together for 10 hours over a boiling water bath. Processing of the reaction mass yielded 5.3 g of the ethyl ether of dimethylethynylcarbinol, with a b.p. of 93-94° at 760 mm; n_D^{20} 1.4050; d_4^{20} 0.8132.

Action of sodium methylate on the allene chloride: 1-chloro-3-methylbutadiene-1,2 in methanol. 15 g of the allene chloride was added to a saturated solution of the methylate, prepared from 4 g of sodium. The reaction mass was then heated to 150° for 10 hours in a sealed tube, nearly the theoretical quantity of sodium chloride, 8.3 g (the theory calling for 8.8 g) being precipitated. Then the whole mixture was treated with water, and the top layer was separated and desiccated with calcium chloride. Fractionation yielded 2.1 g of the methyl ether and several high boiling fractions:

B.p. 56-58° at 110 mm, 97-100° at 760 mm; n_D^{20} 1.4575; d_4^{20} 0.8562; MR_D 31.20; computed 30.62.

0.0976 g substance: 0.2630 g CO_2; 0.0890 g H_2O. Found %: C 73.49; H 10.13; $C_8H_{10}O$. Computed %: C 73.46; H 10.20.

The resulting ether did not form a precipitate when treated with ammoniacal silver nitrate.

Saponification of the ether. 1.5 g of the ether was thoroughly stirred with 20 ml of 5% sulfuric acid for 15 minutes at room temperature, all the ether layer dissolving. 10 ml was driven off from the solution and divided into two parts, 2,4-dinitrophenylhydrazine being added to the first, and semicarbazide

to the second. The 2,4-dinitrophenylhydrazone and the semicarbazone were formed very quickly. After recrystallization from alcohol the 2,4-dinitrophenylhydrazone had a m.p. of 175-176°, while that of the semicarbazone was 219-220°. According to T.A.Favorskaya, the 2,4-dinitrophenylhydrazone of dimethylacrolein melts at 175-176°, while the semicarbazone melts at 223-224° (at 221-222° according to Fisher).

Reaction between dimethylethynylchloromethane and methanol. 150 ml of absolute methanol and 25 g of dimethylethynylchloromethane were poured into a three-necked, round-bottomed flask fitted with a dropping funnel, a mechanical stirrer, and a reflux condenser. A few crystals of phenolphthalein were thrown into the reaction mass, which was then heated to 60° while stirred continuously by the mechanical stirrer. An alcoholic solution of alkali was added a drop at a time from the dropping funnel. The dropping rate was regulated so as to keep the solution at the boundary between the colorless state and a faint pink color. The reaction was continued until the solution acquired a permanent violet color that did not vanish with further heating of the mixture. A total of 80 hours was required for this reaction. The reaction mixture was then fractionated with a Widmer dephlegmator to isolate the isopropenylacetylene, about 1 g of a fraction with a b.p. of 31-34° being recovered. The residue was diluted with water and extracted several times with ether. The ether extracts were combined and desiccated with calcium chloride, after which the ether was driven off into the Widmer dephlegmator, and the residue was fractionated. This yielded 18.5 g of the methyl ether of dimethylethynylcarbinol, with a b.p. of 81-83° at 760 mm; n_D^{20} 1.4005, and 0.9 g of a fraction that distilled at 40-56° at 110 mm, n_D^{20} 1.4110.

Reaction between dimethylethynylchloromethane and ethyl alcohol. This reaction was similar to the preceding one, a solution of 30 g of the chloride in 100 ml of ethyl alcohol being heated to 80°, with constant stirring, over a water bath. The solution turned somewhat yellow during the first 20-30 hours of heating, though it remained transparent and clear enough; the medium was kept neutral, as in the previous experiment, by adding an alcoholic solution of alkali drop by drop in the presence of phenolphthalein. As heating was continued, however, the reaction mixture gradually turned brown. Further alcoholic alkali was added very slowly. Samples of the reaction medium were taken at intervals with a pipet and were tested for their hydrochloric-acid content after they had been diluted with water. The neutrality of the medium could, of course, not be maintained as accurately in this manner as in the preceding reaction. After the reaction was complete, about 1 g of a fraction with a b.p. of 31-35° was driven off from the mixture, while treating the reaction mixture with water followed by fractionating the reaction products yielded 12.7 g of the ethyl ether of dimethylethynylcarbinol. Fractionation of the final residue yielded 0.8 g of a fraction with a b.p. of 103-120° at 30 mm; n_D^{20} 1.4947.

Heating dimethylethynylchloromethane with ethyl alcohol. 20 g of dimethylethynylchloromethane and 30 g of ethyl alcohol were heated together in a sealed tube for 10 hours the solution turning dark brown. The reaction mass was transferred to a flask fitted with a Widmer column and distilled over a water bath. This yielded 12.1 g of a fraction with a b.p. of 20-35° at 760 mm. Refractionation of this fraction yielded 7 g of a fraction with a b.p. of 22-23°, 2.3 g of a fraction with a b.p. of 23-33°, and 2.4 g of isopropenylacetylene, with a b.p. of 33-34° The low-boiling fraction displayed a positive reaction when given the Beilstein test for halogen. We did not investigate this fraction any further. The residue left behind after the low-boiling products had been driven off was diluted with water and extracted with ether. Driving off the ether and fractionating the residue yielded 2.9 g of the ethyl ether of dimethylethynylcarbinol with a b.p. of 93-94°; n_D^{20} 1.4060.

Heating 1-chloro-3-methylbutadiene-1,2 with ethyl alcohol. 20 g of the allene chloride and 30 g of ethyl alcohol were heated to 140° in a sealed tube for 12 hours. Some pressure was found to exist when the tube was opened, while there was a large amount of tar at the bottom of the tube. Fractionation of the reaction mixture yielded 8.3 g of a fraction with a b.p. of 20-38°, most of which distilled at 22-24° when it was redistilled. We were unable to isolate any other reaction products from the mixture.

Action of KOH on dimethylvinylethynylchloromethane in methanol. 25 g of KOH was dissolved in 166 ml of methanol, and 40 g of dimethylvinylethynylchloromethane was added to the resulting solution. The mixture was heated for 4.5 hours over a water bath. Then the reaction mixture was diluted with water and extracted several times with ether. The ether extracts were desiccated with calcium chloride, the ether was driven off, and the residue was fractionated in vacuum with a Widmer column, yielding 7 g of the hydrocarbon 2-methylhexadien-2,5-yne-3, with a b.p. of 42-44° at 60 mm; n_D^{20} 1.4955; and 17.5 g of the methyl ether of dimethylvinylethynyl carbinol, with a m.p. of 59-61° at 48 mm; n_D^{20} 1.4520; d_4^{20} 0.8445. Fractionation of the residue from a small Arbuzov flask yielded 0.7 g of a fraction with a b.p. of 52-55° at 16.5 mm; n_D^{20} 1.4628.

According to I.N.Nazarov [8], 2-methylhexadien-2,5-yne-3 has the following constants: b.p. 46° at 85 mm; n_D^{15} 1.4980; d_4^{20} 0.7960, while those of the methyl ether of dimethylvinylethynylcarbinol are: b.p. 29-30° at 8 mm; n_D^{25} 1.4540; d_4^{18} 0.8497.

Action of sodium ethylate on dimethylvinylethynylchloromethane in methanol. Experiment 1. 8.2 g of sodium was dissolved in 132 ml of absolute methanol, and 40 g of the chloride was added to the solution. The reaction mass was heated for 4.5 hours over a water bath, and then the alcohol was driven off and diluted with water. The upper layer was separated and combined with the ether extracts made from the aqueous layer. The salt residue in the flask was likewise treated with water and extracted with ether. All the ether extracts were combined together and desiccated with calcium chloride, after which the ether was driven off, and the residue was fractionated in vacuum. This yielded 10.3 g of 2-methylhexadien-2,5-yne-3, with a b.p. of 40-41° at 63 mm; n_D^{20} 1.4955; d_4^{20} 0.7832, and 16.4 g of the methyl ether of dimethylvinylethynylcarbinol, with a b.p. of 58-60° at 59 mm; n_D^{20} 1.4520; d_4^{20} 0.8430. Fractionating the residue yielded 0.7 g of a fraction with a b.p. of 58° at 26 mm; n_D^{20} 1.4715.

Experiment 2. A solution of sodium methylate was prepared with 8.2 g of sodium and 89 ml of methanol. 40 g of the chloride was added to the solution, and then the reaction mixture was heated for 5 hours over a water bath. Processing of the reaction mixture yielded 8.7 g of the hydrocarbon, with a b.p. of 39-40° at 61 mm; n_D^{20} 1.4955, and 12.5 g of the methyl ether, with a b.p. of 38-39° at 16 mm; n_D^{20} 1.4520.

Action of sodium acetate upon dimethylvinylethynylchloromethane. 9.2 g of sodium acetate was dissolved in 50 ml of glacial acetic acid, and 25 g of dimethylvinylethynylchloromethane was added to the solution. The mixture was heated to 80° with a reflux condenser for 8 hours. Then the reaction mixture was treated with water, and the resultant upper layer treated with 10% aqueous soda. The aqueous residue left after the reaction mixture had been treated with water was extracted with ether, and the ether extract was added to the separate upper layer. Desiccation and fractionation of the reaction products yielded 3.5 g of the hydrocarbon 2-methylhexadien-2,5-yne-3, with a b.p. of 32° at 42 mm; n_D^{20} 1.4938, and 8.4 g of the acetate of dimethylvinylethynylcarbinol, with a b.p. of 70-72° at 16 mm; n_D^{20} 1.4639; d_4^{20} 0.9404.

In a second test, 46.6 g of potassium acetate and 50 g of the chloride

were heated together in 100 ml of glacial acetic acid. Processing of the reaction mixture yielded 1.7 g of the hydrocarbon, with a b.p. of 27-31° at 40 mm; n_D^{20} 1.4960, and 23.8 g of the acetate of dimethylvinylethynylcarbinol, with a b.p. of 62-63° at 10 mm; n_D^{20} 1.4625; d_4^{20} 0.9404.

According to I.N.Nazarov [2], the acetate of dimethylvinylethynylcarbinol he secured by reacting the dimethylvinylethynylcarbinol with acetic anhydride in sulfuric acid had the following constants: b.p. 59-60° at 7 mm; n_D^{15} 1.4650; d_4^{15} 0.9453.

Saponification of dimethylvinylethynylchloromethane. 150 ml of water, 60 g of calcium carbonate, and 60 g of the chloride were placed in a flask fitted with a reflux condenser and a mechanical stirrer. The reaction mixture was stirred for 30 hours at room temperature, all the chloride entering solution. The resulting solutions was repeatedly extracted with ether, the ether extract was desiccated with sodium sulfate, the ether was driven off, and the residue was distilled in vacuum.

This yielded 31.7 g of dimethylvinylethynylcarbinol, with a b.p. of 60° at 15 mm; n_D^{20} 1.4755.

SUMMARY

1. Reacting alcoholic solutions of alcoholates and an alcoholic alkali with dimethylethynylchloromethane and dimethylvinylethynylchloromethane under conditions that favor a bimolecular reaction yielded ethers of dimethylethynylcarbinol and dimethylvinylethynylcarbinol and isopropenylacetylene and isopropenylvinylacetylene, respectively.

2. The reaction of the same reagents with the allene chloride 1-chloro-3-methylbutadiene-1,2 in methanol resulted in a low yield of the methyl ether of 1-methoxy-3-methylbutadiene-1,2.

3. The monomolecular alcoholysis of dimethylethynylchloromethane yielded ethers of dimethylethynylcarbinol plus a negligible amount of isopropenylacetylene.

LITERATURE CITED

[1] A.N.Pudovik and B.A.Arbuzov, Bull. USSR Acad. Sic., Div. Chem. Sci., 1947, No. 4, 377; A.N.Pudovik, Ibid., 1948, No. 5, 529; A.N.Pudovik, Ibid., 1949, No. 1, 83; A.N.Pudovik and V.I.Nikitina, J.Gen.Chem. 19, 75 (1949).

[2] I.N.Nazarov, Bull. USSR Acad. Sci., Div. Chem. Sci., 1938, 699.

[3] E.Hughes, C.Ingold, Mastermann, and M.Nulty, J.Chem.Soc., 1940, 899.

[4] T.A.Favorskaya, J.Gen.Chem. 9, 389 (1939).

[5] A.E.Favorsky, J.Russ.Chem.Soc. 33, 357 (1901); 37, 643 (1905); Certificate of Authorship No. 31,017.

[6] J.Am.Chem.Soc. 71, 398 (1949).

[7] J.Am.Chem.Soc., 72, 3542 (1950).

[8] I.N.Nazarov, Bull. USSR Acad. Sci., Div. Chem. Sci., 1938, 709.

Received June 15, 1949.

Laboratory of Organic Chemistry,
University of Kazan

See C. B. Translation, page 67.

ACETYLENE - ALLENE REARRANGEMENTS

III. The Action of Organomagnesium Compounds on Dimethylvinylethynylchloromethane

A. N. Pudovik and L. A. Mukhamedova

The action of organomagnesium compounds upon allyl halogen isomers has been investigated fairly thoroughly by now. Prevost and Kirrman, who were the first to explore such reactions, believed that they are ionic. They offered no proof, however, of the ionic nature of these reactions; in most instances they investigated the reaction of organomagnesium compounds with some one of the allyl halogen compounds, from which no conclusions could be inferred regarding the nature of the reactions. This proof has been adduced by one of the present authors in a more rigorous form: a mixture of nearly identical methoxyphenylpentenes was secured by reacting phenylmagnesium bromide with isomeric methoxychloropentenes. Reacting various organomagnesium compounds with isomeric ethoxy chloropentenes yielded ethoxy alkyl pentenes, with structures conforming to those of the original chloride [1].

In the course of these researches the interesting question arose of exploring the reactions of organomagnesium compounds with acetylenic and allenic chlorides, ascertaining the feasibility of carrying out acetylene-allene rearrangements during these reactions, and determining the nature of the latter. Reaching these objectives involved much more difficulty than was the case for the allyl isomers, inasmuch as the investigation of their reactions is practically confined to compounds of the acetylenic halogen type (allene halogen compounds not being reactive), while separation of the resultant isomeric hydrocarbons by fractionation is practically impossible because of their close boiling point. We had to resort to oxidation or ozonation on the whole to judge the composition of the products.

There is a recent paper by A.I.Zakharova [2] in the literature, dealing with reactions of organomagnesium compounds with acetylene halogen compounds. By reacting methylmagnesium bromide with 2-chloro-2-methylpentyne-3, for example, she secured a product with a b.p. of 82-84°, which was recognized from the oxidation data to be nonhomogeneous, consisting of tetramethylallene and a much smaller proportion of methyl-tert-butylallene.

A.I. Zakharova is of the opinion that the formation of anomalous reaction products is not due to subsequent isomerization of the normal product initially formed from the chloride and the organomagnesium compound, but is rather the result of intramolecular rearrangement at the instant of reaction. Nor does she reject the possibility that the reactions she investigated are ionic, like the reactions of allyl compounds.

We have made a study of the reaction of phenylmagnesium bromide and ethyl magnesium bromide with dimethylvinylethynylchloromethane. Reacting phenylmagnesium bromide with dimethylvinylethynylchloromethane yielded a product that had the following constants after refractionation: b.p. 94-96° at 7 mm;

n_D^{20} 1.5390; d_4^{20} 0.9223.

Oxidation of the resultant product with potassium permanganate yielded acetone, benzoic acid, and dimethylphenylacetic acid. The acetone was identified as its semicarbazone, the benzoic acid by its melting point, and the dimethylphenylacetic acid by its boiling point, its decomposition by sulfuric acid (evolving a large amount of carbon monoxide), and analysis of its silver salt. We concluded from the oxidation findings that the product of the reaction between phenylmagnesium bromide and dimethylvinylethynylchloromethane is not an individual compound, but rather a mixture of isomeric acetylene and allene hydrocarbons.

As for the nature of the reaction involved, our results do not enable us to furnish a complete picture of the process, though we can assert with confidence that the allene hydrocarbon is formed in a monomolecular reaction, involving the intermediate formation of a carbonium ion.

The mechanism involved in the formation of the acetylene hydrocarbon – 2-methyl-2-phenylhexen-5-yne-3 – is less apparent: it may be formed either in a monomolecular reaction or a bimolecular reaction or, again, by the two conjointly; our experimental results allow of no definite conclusions upon this point.

We likewise made a study of the reaction of dimethylvinylethynylchloromethane with ethylmagnesium bromide. Here again, we secured only a single hydrocarbon with a b.p. of 43-44.5° at 30 mm; n_D^{20} 1.4630; d_4^{20} 0.7782, though oxidizing it with potassium permanganate enabled us to secure and identify the following products: acetone and formic and dimethylethylacetic acids. The acetone was identified by preparing its semicarbazone, the formic acid by its constants and by reducing it with silver oxide and mercuric chloride, and the dimethylethylacetic acid by its constants. A more detailed analysis of the dimethylethylacetic acid fraction disclosed, however, that it was not homogeneous, containing a minute quantity of 2-ketobutyric acid. This was shown by the fact that the product displayed positive, even though not very pronounced, reactions for a carbonyl group with sodium nitroprusside, β-naphthol, and ammoniacal silver nitrate. It was impossible to separate the two acids, owing to the closeness of their boiling points; analysis of the silver salt gave values that lay in between those calculated for the two acids.

Ozonation of the product likewise failed to give precise results, yielding formic acid, oxalic acid, and dimethylethylacetic acid, the latter contaminated with traces of formic acid and possibly of α-ketobutyric acid.

Our findings indicate that the reaction of ethylmagnesium bromide with dimethylvinylethynylchloromethane involves a partial acetylene-allene rearrangement, as was the case with benzenemagnesium bromide. The reaction involving the rearrangement is doubtless monomolecular.

EXPERIMENTAL

Action of benzenemagnesium bromide on dimethylvinylethynylchloromethane. To an ether solution of benzenemagnesium bromide, prepared with 10.8 g of magnesium and 70 g of bromobenzene in 150 ml of absolute ether, 50 g of dimethylvinylethynylchloromethane was added drop by drop, with constant stirring by a mechanical stirrer and water-cooling. The reaction involved the evolution of considerable heat. After all the chloride had been added, the contents of the flask solidified to a gelatinous mass. The reaction mixture was heated to 60° for 4 hours over a water bath. Then it was treated with water and dilute hydrochloric acid, and the ether layer was separated and desiccated with calcium chloride. The residue left after the ether had been driven off was fractionated from an Arbuzov flask with pyrogallol added, yielding the following fractions:

B.p. 75-94° at 7 mm – a few drops; b.p. 94-96° at 7 mm – 14.8 g; b.p. 96-112° at 7 mm – 2.2 g; the residue consisted of a large amount of tar. The constants of the second fraction were as follows after refractionation with a Widmer dephlegmator:

B.p. 94-96° at 7 mm; n_D^{20} 1.5390; d_4^{20} 0.9223; MR_D 57.73; computed for $C_{13}H_{14}$ 56.16; for $C_{13}H_{14}$ 57.23.

0.0919 g substance: 0.3080 g CO_2; 0.0684 g H_2O. 0.0912 g substance: 0.3046 g CO_2; 0.0676 g H_2O. Found %: C 91.41; 91.14; H 8.83, 8.29. $C_{13}H_{14}$. Computed %: C 91.77; H 8.23.

Oxidation of the hydrocarbon with a b.p. of 94-96° at 7 mm. 7.9 g of the hydrocarbon was added to 300 ml of water, and pulverized potassium permanganate was added to the resulting mixture a little at a time, with vigorous stirring and cooling by running water, a total of 40 g being added. The reaction mixture was allowed to stand overnight at room temperature, after which it was transferred to a round-bottomed flask, and about 40 ml of the solution was distilled off. The distillate was desiccated with potash, and some 15 ml of the solution was redistilled from it. The new distillate had the characteristic odor of acetone: the semicarbazone was precipitated when semicarbazide was added to it. Recrystallized from methanol, the semicarbazone had a m.p. of 189-190° and exhibited no depression of the melting point when mixed with the semicarbazone of pure acetone.

After the neutral products had been driven off and the manganese dioxide had been filtered out, the aqueous salt solution was evaporated almost to dryness, the salts were decomposed with dilute sulfuric acid, and the organic acids were extracted repeatedly with ether. The ether extract was desiccated with calcium chloride, the ether was driven off, and the residue was fractionated in vacuum, yielding two fractions: b.p. 140-146° at 12 mm – 3.4 g; and b.p. 146-150° at 12 mm – 3.1 g. Fraction 1 consisted mainly of benzoic acid (m.p. 120-121°). The second fraction was chilled for a long time at 0°, turning into a thick oily liquid containing a few crystals of benzoic acid. The crystals were filtered out out, and the liquid was tested for its dimethylphenylacetic acid content by heating it with concentrated sulfuric acid.

In conformity with the data in the literature, heating turned the solution yellow, carbon monoxide being liberated violently for a long time. When ignited, the carbon monoxide burned with a small blue flame. The boiling point of the fraction, 146-150 mm at 10 mm, conformed to the figure given in the literature for dimethyl-phenylacetic acid.

By way of conclusively proving the presence of dimethylphenylacetic acid in this fraction, we neutralized it with ammonium carbonate and precipitated it fractionally with silver nitrate. This yielded three silver salt fractions. The analyses of the second and third silver salt fractions corresponded to that of dimethylphenylacetic acid.

0.1299 g salt: 0.0508 g Ag. 0.1260 g salt: 0.0496 g Ag. Found %: Ag 39.10, 39.37. $C_{10}H_{11}O_2Ag$. Computed %: Ag 39.84.

Analysis of the first fraction indicated a much higher percentage of silver, apparently because of the presence of a trace of silver benzoate.

Action of ethylmagnesium bromide on dimethylvinylethynylchloromethane. 50 g of dimethylvinylethynylchloromethane was gradually added, with water-cooling and constant stirring, to an ether solution of ethylmagnesium bromide, prepared with 11.1 g of magnesium, 50 g of ethyl bromide, and 150 ml of absolute ether. The reaction was very intense, much heat being evolved. After all the chloride

had been added, the reaction mass was heated to 60° for 3 hours over a water bath. Then it was processed as in the preceding experiment. The ether extract was filtered and desiccated, and the ether was driven off, the residue being fractionated from an Arbuzov flask containing pyrogallol. Three fractions were collected: b.p. 30-43° at 30 mm – a few drops; b.p. 43-46° at 30 mm – 21.7°; b.p. up to 50° at 10 mm – 3.1 g; the flask contained considerable tar as a residue. Refractionation of these fractions yielded a substance with the following constants:

B.p. 43-44.5° at 30 mm; n_D^{20} 1.4630 d_4^{20} 0.7782; MRD 43.17; computed for $C_8H_{14}F_2$: 42.36, for $C_8H_{14}F_2$ 41.29. 0.0892 g substance: 0.2888 g CO_2; 0.0904 g H_2O. Found %: C 88.28; H 11.34. C_8H_{14}. Computed %: C 88.52; H 11.47.

Oxidation of the hydrocarbon with potassium permanganate. 76 g of pulverized potassium permanganate was gradually added, with chilling and vigorous stirring, to 11 g of the hydrocarbon in 600 ml of water. After all the permanganate had been added, which took 2.5 hours, the reaction mass was set aside to stand for 24 hours at room temperature. The supernatant solution above the manganese dioxide clarified. The reaction mass together with the manganese dioxide precipitate was transferred to a round-bottomed flask, and about 20 ml of distillate was distilled from it with steam. The distillate had the characteristic odor of acetone, while adding free semicarbazide to it quickly threw down the acetone semicarbazone. After recrystallization from methanol the semicarbazone had a melting point of 188-190° and exhibited no depression of the melting point when mixed with a semicarbazone prepared from pure acetone. After the manganese dioxide had been filtered out, the filtrate was evaporated to dryness, and the salts of the organic acids were decomposed with dilute sulfuric acid and extracted with ether. The ether extract was desiccated with calcium chloride, the ether was driven off, and the residue was distilled from an Arbuzov flask at atmospheric pressure. Three fractions were collected: b.p. 101-108° – 2 g; b.p. 108-180° – 0.3 g; and b.p. 180-192° – 4.0 g. The first fraction had a b.p. of 100-102° after redistillation and proved to be formic acid. When it was added to ammoniacal silver nitrate a black precipitate of silver was thrown down, while adding it to a solution of mercuric chloride threw down a white precipitate of calomel. Refractionation of the second and third fractions with a Widmer column yielded a fraction with a b.p. of 186-188°, n_D^{20} 1.4168, the constants of which approximated dimethylethylacetic acid. Further investigation of this substance demonstrated, however, that it was not homogeneous, but apparently contained a trace of α-ketobutyric acid, since it displayed a positive, even though not very marked reaction for the presence of a carbonyl group. Adding the substance to a solution of sodium nitroprusside turned the solution red, while adding it to a solution of β-naphthol in concentrated sulfuric acid turned the solution orange-red. Heating the substance with ammoniacal silver nitrate coated the test tube walls with a small silver mirror. We were unable to separate the two acids owing to the proximity of their boiling points. Analysis of the silver salt yielded a percentage of silver that was intermediate between those calculated for dimethylethyl acetic and α-ketobutyric acids.

Ozonation of the hydrocarbon. A current of ozonized oxygen was passed through a solution of 10 g of the hydrocarbon in 70 ml of chloroform for 23 hours. The chloroform was driven off in vacuum, and the residual ozonide, a thick transparent resin, was decomposed by heating it with 30 ml of water for 5 hours and then with hydrogen peroxide present for another 6 hours. The volatile products were driven off together with the water, first at atmospheric pressure and then in a slight vacuum. The residue, which was a tarry mass, was boiled with water. After most of the water had been boiled away, crystals of oxalic acid settled out of the remaining solution; they had a melting point of 198-199° after

recrystallization from water and exhibited no depression of the melting point when mixed with pure oxalic acid. The aqueous solution of the volatile acids was neutralized with soda and then evaporated almost to dryness, the salts being decomposed with dilute sulfuric acid, and the free acids extracted with several batches of ether. After the ether extract had been desiccated and the ether driven off, the residue was fractionated at atmospheric pressure, yielding two fractions: b.p. 100-107° – 3 g; and b.p. 120-177° – 1.9 g. The first fraction was formic acid, as was proved by a series of qualitative reactions. Refractionation of the second fraction yielded another 1.1 g of formic acid and 0.4 g of a substance with a b.p. of 178-185°, n_D^{20} 1.4135. The constants of the latter product resembled those of dimethylethylacetic acid, but the product contained a slight trace of formic acid, as was readily apparent from its odor, and possibly α-ketobutyric acid as well, since it exhibited a somewhat high silver content upon analysis of its silver salt.

SUMMARY

A study has been made of the reactions of dimethylvinylethynylchloromethane with ethylmagnesium and phenylmagnesium bromides. The results of oxidizing the reaction products indicate that both reactions involve a partial acetylene – allene rearrangement. A suggestion is put forward to explain the mechanism of this rearrangement.

LITERATURE CITED

[1] A.N.Pudovik and G.M.Vinokurova, J.Gen.Chem. 19, 1882 (1949).*

[2] A.I.Zakharova, J.Gen.Chem. 17, 1277 (1947); 19, 1297 (1949).**

Received June 15, 1949.

Laboratory of Organic Chemistry,
University of Kazan

* See C.B. Translation, p. 3-345 ff.

** See C. B. Translation, p. 1293 ff.

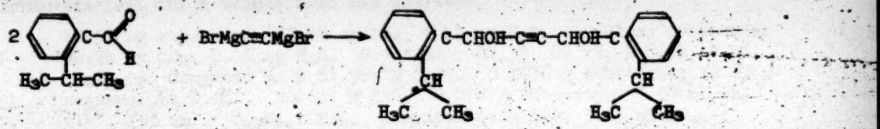
THE ADDITION OF HYDROGEN TO AN ACETYLENE DERIVATIVE.

CATALYTIC HYDROGENATION OF o-DICUMINYLBUTYNEDIOL

I. M. Gverdtsiteli and Sh. G. Mikadze.

Yu.S.Zalkind [1] and his pupils repeatedly noticed that when γ-acetylenic glycols were hydrogenated in the presence of colloidal palladium, the rate at which hydrogen was added dropped sharply after the addition of two atoms of hydrogen, the rate of hydrogenation being affected by the weight, the volume, and the structure of the glycol. According to Yu.S.Zalkind [2], this sharp drop in the hydrogenation rate was due to the formation of a hydrogen bond.

In the present research we have endeavored to make a study of the rate of hydrogenation of o-dicuminylbutynediol. No research had been done on the hydrogenation of a glycol of this structure, so that we were interested in observing its behavior in catalytic hydrogenation. We synthesized the o-dicuminylbutynediol by a Iotsich reaction from o-cumaldehyde and acetylenedimagnesium dibromide:



the yield being 36.8% of the theoretical. This glycol consists of white crystals with a m.p. of 117.5-119° (from petroleum ether). The behavior of o-dicuminylbutynediol in catalytic hydrogenation is like that of other disecondary and ditertiary glycols, i.e., hydrogenation slows down markedly in the presence of palladium after two atoms of hydrogen have been added, whereas there is no break in the hydrogenation rate when platinum is employed. Comparing the hydrogenation rate with that for diphenylbutynediol (Table 1) and for sym-dimethyldiphenylbutynediol, we see that o-dicuminylbutynediol is hydrogenated much more slowly than diphenylbutynediol, which may be attributable to steric hindrances. The rate at which o-dicuminylbutynediol is hydrogenated rises as the amount of catalyst employed is increased (Table 2).

TABLE 1

No.	Glycol	Reaction temperature	Amount of glycol, moles	Ml of solvent	Mg of palladium	Hydrogenation time, minutes
1	$C_6H_5CHOHC{\equiv}CCHOHC_6H_5$	16°	0.01	50	5	5
2	$(CH_3)_2CHC_6H_4CCH(OH)C{\equiv}C$ $(CH_3)_2CHC_6H_4CCH(OH)C{\equiv}C$	26	0.005	50	5	60

1608- 160

TABLE 2

Effect of the Amount of Catalyst Used Upon the Hydrogenation of o-Dicuminylbutynediol

No.	Mg. of catalyst	Ml of hydrogen added in ... minutes:								
		1.5	3	6	9	12	15	18	21	60
1	5	-	14	25	35	45	54	62	70	138
2	10	-	27	61	92	117	140	-	-	-
3	200	110	184	208	-	-	-	-	-	-

EXPERIMENTAL

Synthesis of o-dicuminylbutynediol. 30 g of o-cumaldehyde was added, with chilling and constant stirring, to acetylenedimagnesium dibromide, prepared in the usual manner from 8 g of metallic magnesium, 37 g of ethyl bromide, and acetylene. Seventy-two hours later the mixture was decomposed, first with water, and finally with water acidulated with sulfuric acid. The reaction products were extracted with ether. The solution was desiccated with anhydrous sodium sulfate, and the ether driven off, leaving behind a brown mass that crystallized with difficulty. Treatment with petroleum ether yielded 12 g of white crystals with a m.p. of 117.5-119°, representing a yield that was 36.8% of the theoretical. The crystals were freely soluble in alcohol and ether, and slightly soluble in benzene and petroleum ether. The substance colored concentrated sulfuric acid red. The Bukhovets test for a triple bond was positive.

12.34 mg substance: 37.24 mg CO_2; 9.17 mg H_2O. 12.21 mg substance: 36.74 mg CO_2; 9.12 mg H_2O. Found %: C 82.35, 82.12; H 8.31, 8.35. $C_{22}H_{26}O_2$. Computed %: C 81.98; H 8.07. 0.1076 g substance; 19.89 g benzene: Δt 0.08°. Found: M 336. 0.020 g substance: 3.00 ml CH_4 (14°, 733 mm). $C_{22}H_{24}(OH)_2$. Computed %: M 322, 3.03 ml CH_4.

Catalytic hydrogenation of o-dicuminylbutynediol. Colloidal palladium on wheat starch was employed as the catalyst, 1 ml of aqueous solution containing 2 mg of palladium. The activity of the catalyst was tested by hydrogenating tetramethylbutynediol; the reaction took 5 minutes for 0.01 mole of this glycol, when 5 mg of palladium was used.

Experiment 1. 1.61 g of the glycol (0.005 mole), 5 mg Pd, 50 ml C_2H_5OH; 26°, 730 mm; H_2 130 ml.

t	3	6	9	12	15	18	21	60
v	14	11	10	10	9	8	8	
V	14	25	35	45	54	62	70	138
% H_2	10.77	19.2	26.9	34.6	41.6	47.7	58.8	

Experiment 2. 1.61 g of the glycol, 10 mg Pd, 50 ml C_2H_5OH; 26°, 730 mm; H_2 130 ml.

t	3	6	9	12	15
v	27	34	31	25	23
V	27	61	92	117	140
% H_2	20.78	46.9	70.77	90	

Experiment 3. 1.61 g of the glycol. 200 mg Pd, 50 ml C_2H_5OH; 26°, 730 mm; H_2 130 ml.

t	1.5	3	4.5	6
v	110	74	24	18
V	110	184		
% H_2	84.6			

Hydrogenation of the o-dicuminylbutynediol with platinum indicated that the reaction was different from what occurred when palladium was used: hydrogen was added unevenly, resulting in the formation of a saturated glycol.

Experiment 4. 1.61 g substance. 0.736 g Pt, 50 ml C_2H_5OH; 26°, 730 mm; $2H_2$ 260.

t	3	6	9	12	15	18	21
v	60	62	55	42	40	26	4
V	60	122	177	219	259	285	289
% H_2	23.07	47.0	68.08	84.2			

Analysis of the hydrogenation products. After two atoms of hydrogen had been added to the o-dicuminylbutynediol, the palladium was filtered out, the alcohol was driven off, and the remaining liquid was crystallized into white crystals. Recrystallization from petroleum ether yielded white crystals with a m.p. of 123-125°, the overall yield being 40.37%. The crystals turned concentrated sulfuric acid crimson.

0.0106 g substance: 0.1088 g camphor: Δt 11.2°. Found: M 324.75. 0.0560 g substance: 9.20 ml (CH_4 27°, 727.5 mm). $C_{22}H_{28}(OH)_2$. Computed: M 324.00; 8.94 ml CH_4. 9.78 mg substance: 29.17 mg CO_2; 7.58 mg CO_2; 7.58 mg H_2O. 12.13 mg substance: 36.11 mg CO_2; 9.39 mg H_2O. Found %: C 81.39, 81.24; H 8.45, 8.65. $C_{22}H_{28}O_2$. Computed %: C 81.46; H 8.64.

The saturated glycol – o-dicyminylbutanediol – was secured by processing the product of the hydrogenation of the acetylenic glycol with platinum, yielding crystals with a m.p. of 103-105°. The yield was 43.47%. It did not color concentrated sulfuric acid.

0.0395 g substance: 0.1075 g camphor: Δt 10.5°. Found: M 336.5. 0.0630 g substance: 10.35 ml CH_4 (26.5°, 780 mm). $C_{22}H_{28}(OH)_2$. Computed: M 326; 9.90 ml CH_4. 9.41 mg substance; 27.99 mg CO_2; 8.00 mg H_2O. 9.19 mg substance: 27.31 mg CO_2; 7.90 mg H_2O. Found %: C 81.17, 81.09; H 9.51, 9.61. $C_{22}H_{30}O_2$. Computed %: C 80.98; H 9.20.

SUMMARY

The acetylenic glycol o-dicuminylbutynediol has been synthesized for the first time, the rate at which hydrogen is added with colloidal palladium and platinum black being measured, and the influence of the glycol structure upon the rate of hydrogenation being demonstrated. The ethylenic glycol o-dicuminylbutenediol and the saturated glycol o-dicuminylbutanediol have been synthesized for the first time.

LITERATURE CITED

[1] Yu.S.Zalkind, J.Gen.Chem., 5, 1723 (1935); Zalkind and assoc., J.Russ. Chem. Soc. 47, 480 (1915); J.Gen. Chem. 9, 855 (1939); J.Gen.Chem. 5, 1725 (1935); J.Gen.Chem. 8, 1382 (1938).

[2] Yu.S.Zalkind, J.Gen.Chem., 18, 2149 (1948).

Received October 21, 1949.

Laboratory of Organic Chemistry,
The J V.Stalin State University of
Tbilisi

THE CONDENSATION OF FORMALDEHYDE WITH SODIUM BUTYLATE

V. I. Lyubomilov and A. P. Terentyev

In 1948 Gorin [1] advanced the following set of reactions for the formation of divinyl from alcohol with a Lebedev catalyst:

$$CH_3{-}CH_2OH \longrightarrow CH_3{-}CHO + H_2.$$

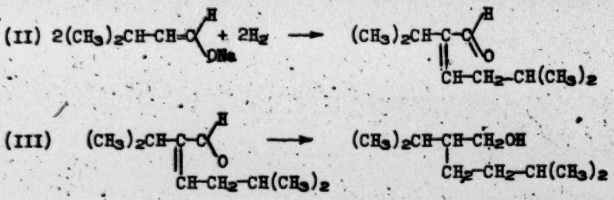
$$CH_3{-}CHO + CH_3{-}CHO \rightarrow [CH_3{-}CHOH{-}CH_2{-}CHO] \rightarrow H_2O + CH_3{-}CH{=}CH{-}CHO.$$

$$CH_3{-}CH{=}CH{-}CHO + H_2 \longrightarrow CH_3{-}CH{=}CH{-}CH_2OH;$$

$$CH_3{-}CH{=}CH{-}CH_2OH \longrightarrow H_2O + CH_2{=}CH{-}CH{=}CH_2.$$

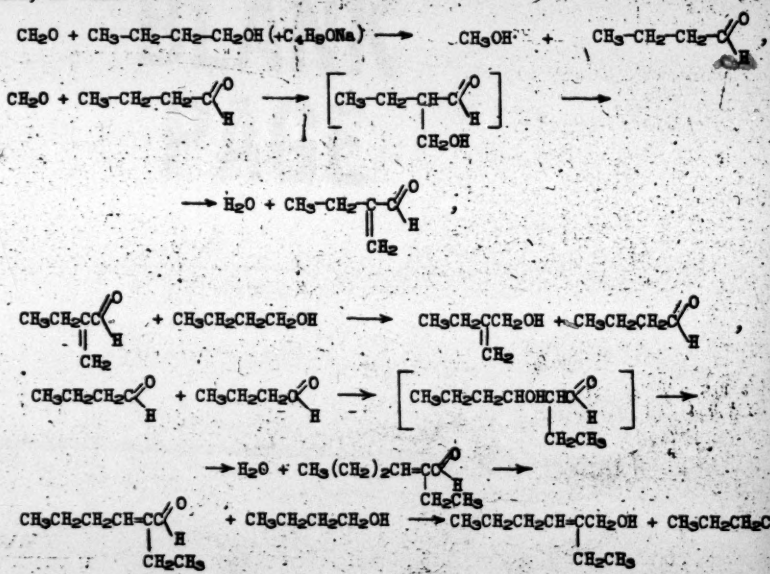
A similar sequence was put forward by Kagan and his associates [2], who pointed out that ethyl alcohol is a hydrogen donor in the conjugated hydrogenation reaction of crotonaldehyde. Gorin and his associates [3] extended this set of reactions to other alcohols, securing the very hydrocarbons whose formation corroborated the foregoing scheme for the formation of divinyl from a mixture of alcohols or a mixture of alcohols with aldehydes or ketones. In this set of reactions, one of the intermediates in the synthesis of the diene hydrocarbons is an unsaturated alcohol. Whenever a single alcohol or an alcohol plus its corresponding aldehyde is used for the reaction, as is the case in the synthesis of divinyl (by the Lebedev or Ostromyslensky method), hydrogenation of this unsaturated alcohol yields an alcohol with double the number of hydrogen atoms. And, in fact, the products recovered in the synthesis of divinyl usually include both crotyl and butyl alcohols. This reaction is, therefore, essentially an alcohol condensation, the temperature conditions and the catalyst compelling the bulk of the reaction product to change into a diene hydrocarbon. The reaction involved in the formation of higher alcohols from lower ones, which takes place under quite different conditions, was discovered in 1889 by Markovnikov and Zubov [4], who observed that the reaction of methylhexylcarbinol with KOH powder at high temperature yielded the alcohol $C_{24}H_{50}O$. In an extensive series of subsequent papers Guerbet [5], and later Weizmann [6] investigated this reaction at length with various alcohols and their mixtures. In 1924 one of the present authors [7] condensed a number of alcohols by passing alcohol vapors over the respective magnesium alcoholates at 400°. There are, moreover, patents on the synthesis of the higher alcohols from the lower ones in the gas phase [8]. In 1931 Hückel and Naab [9] proposed the following set of reactions for this condensation, using isoamyl alcohol as an example:

$$\text{(I)} \quad (CH_3)_2CH{-}CH_2{-}CH_2ONa \longrightarrow (CH_3)_2CH{-}CH{=}C\begin{matrix}H\\ ONa\end{matrix} + H_2$$



The step-by-step oxidation exchange between the carbonyl compound and the alcoholate in an excess of the initial alcohol should have yielded an unsaturated alcohol in stage (III) of this condensation series, though there is no mention of the formation of any but saturated alcohols. In the analogous reactions for the formation of divinyl from alcohol cited previously, the formation of an unsaturated (crotyl) alcohol is actually proved by its detection among the reaction products.

We have investigated the action of an aldehyde upon a solution of an alkali metal alcoholate in the corresponding alcohol. In this simpler reaction we might have expected the formation of the corresponding unsaturated alcohols. Passing gaseous formaldehyde through a hot solution of sodium butylate in butyl alcohol, we expected to secure a mixture of 2-ethylpropenol and 2-ethyl-3-propylallyl alcohol, as follows:



Rectification of the reaction product with a packed column one and a half meters high yielded a fraction with a b.p. of 127-133°, which upon refractionation yielded the non-homogeneous fractions 9 to 13 (cf Table), with b.p. ranging from 126 to 133.5°. The gradual rise in the boiling points, the refractive indexes, and the bromine numbers of these fractions indicate that the 2-ethylpropenol

is actually concentrated in these fractions, but that the latter also contain a saturated alcohol with a molecular weight and a boiling point that closely approximate those of 2-ethylpropenol.

We assumed that it was 2-methylbutanol-1, the hydrogenation product of 2-ethylpropenol [14]. We were actually able to isolate and identify 2-methylbutanol in Fraction 9 by oxidizing the unsaturated alcohol with permanganate. The proximity of the boiling point of 2-ethylpropenol to that of 2-methylbutanol did not

Rectification of the Reaction Product

Fraction No.	Grams	Boiling point (°)	n_D^{20}	Bromine No., mg.
1	25.4	64-65°	1.3305	-
2	5.3	65-92.5	1.3612	-
3	Oil layer 468.0	92.5	1.3914	3
	Aqueous layer 218.0			
4	24.4	92.5-116.3	1.3985	-
5	774.4	116.3-117.5	1.4000	15
6	8.7	117.5-118	1.4010	37
7	14.0	118-121	1.4050	144
8	7.5	121-126	1.4132	464
9	13.4	126-127	1.4200	818
10	13.1	127-129	1.4260	1170
11	13.4	129-132	1.4290	1390
12	9.8	132-133	1.4320	1475
13	8.4	133-133.5	1.4336	1640
14	6.0	133.5-170	1.4342	-
15	2.2	170-184	1.4400	1144
16	6.0	184-250	1.4410	581
17	10.3	Above 250	1.4362	150

allow us to secure the former in the pure state. Of the fractions, only Fraction 13 contained 90% of this alcohol (the percentage being determined from the double bonds). We made use of Kondakov's indication [11] that 2-ethylpropenol is isomerized to 2-methylbutanal when it is heated with dilute sulfuric acid in order to prove its presence in the fractions collected. The aldehyde was formed very readily when Fractions 11, 12, and 13 were heated with 0.1 N sulfuric acid, though the 2,4-dinitrophenylhydrazone prepared from the aldehyde fused at 128.2°, whereas Morgan and Hardy [12] give a m.p. of 119-120.5° for this derivative of 2-methylbutanal. Supposing that the figure given by Morgan and Hardy was in error, we effected an organomagnesium synthesis of 2-methylbutanal. The 2,4-dinitrophenylhydrazone prepared from the latter had a melting point of 128.5-128.8° and exhibited no depression with our test sample; the dimedon derivative had a melting point of about 135°. Another proof that Fractions 9-13 are a mixture of 2-methylbutanol and 2-ethylpropanol yields pure 2-methylbutanol. Hence, reacting formaldehyde with a solution of sodium butylate in butyl alcohol at high temperature yields 11% of theory of 2-ethylpropanol and about 3% of theory of 2-methylbutanol, in terms of CH_2O. According to the set of reactions cited above, we might also expect 2-ethyl-3-propylallyl alcohol to be formed. It is apparent from the foregoing that the impurity in it may be its reduction product, that is, 2-ethylhexyl alcohol. To judge from the boiling point and the results of bromination, Fraction 15 might be such a mixture. Analysis of this fraction indicated, however, that it is an intermediate fraction, containing only a small quantity of the alcohols specified.

EXPERIMENTAL

1444 g of butanol, previously washed with a $KMnO_4$ solution, desiccated, and triply distilled (negative test for unsaturated hydrocarbons) was placed in a flask fitted with a stirrer, a thermometer, and a reflux condenser, one end of which was connected to a gasometer. 150 g of sodium was dissolved in the butanol. After the sodium had dissolved, 221.5 g of gaseous formaldehyde, prepared by evaporating paraform in a flask connected to a wide tube immersed in the liquid contained in the reaction flask, was passed through the solution for 7 hours 45 minutes at 120°, 0.38 liter of hydrogen was collected in the gasometer while the CH_2O was passed through the solution. The reaction product was then distilled with steam, the condensate containing 1614 g in the alcoholic layer and 1037 g in the aqueous one. The distilling flask contained a residue of 2710 g of an aqueous-alkaline salt solution and 30 g of a brown oily substance.

Determination of the unsaturated hydrocarbons in the alcoholic layer of the condensate. Titration of an acidulated alcoholic solution of a weighed sample with a bromide-bromate solution (1 ml of solution equivalent to 40.24 mg of bromine).

2.625 g substance: 5.5 ml bromide-bromate mixture. Found: bromine number 84.6 mg bromine per g substance.

After a series of separate rectifications of the aqueous and alcoholic layers of the condensate and desiccation of the intermediate fractions with potash or copper sulfate (with the sole exception of the butanol fractions), we secured the 17 fractions listed in the table.

Analysis of the Fractions

Fraction 1. B.p. 64-65°; d_4^{20} 0.7936; n_D^{20} 1.3305. Methyl alcohol. The acid phthalate, with a m.p. of 82-83°, was prepared. Fractions 2-7. To judge by the boiling points and the refractive indexes, these fractions constituted aqueous and anhydrous butanol. In order to prove that the next fractions, up to Fraction 13 inclusive, consisted of a mixture of 2-methylbutanol and 2-ethylpropenol, they were analyzed thoroughly. Fraction 8 was brominated, yielding a bromide that proved to be, upon analysis, the expected dibromide of 2-ethylpropenol. 2.8 g of bromine was added a drop at a time to 5.6 g of Fraction 8, chilled with ice, and the resultant product was distilled in vacuum (7.5 mm), the receiver being chilled with a freezing mixture. The following fractions were collected: I – 2.8 g; n_D^{20} 1.4108. (It distilled at 105-127° at 736 mm pressure); II – 1.2 g, up to 38°; n_D^{20} 1.4355; III – 0.8 g, 38-103°; n_D^{20} 1.4632; IV – 2.15 g, 103-106°; n_D^{20} 1.5320; and a residue of 1.5 g; n_D^{20} 1.5240. All the fractions gave a positive Beilstein test for halogen, Fraction IV being an oily liquid with the odor of camphor. The bromine in Fraction IV was determined by the Stepanov method.

0.2707 g substance: 22.10 ml 0.1 N $AgNO_3$. Found %: Br 65.25.
$C_5H_{10}OBr_2$. Computed %: Br 64.99.

Recovery of 2-methylbutanol from Fraction 9. 10.0 g of the fraction and 200 ml of water were placed in a flask fitted with a stirrer and chilled to 2-3°, after which 29 g of $KMnO_4$ was gradually added. The neutral products were extracted with ether, and the ether driven off. Repeated distillation yielded 2.8 g of an alcohol with a b.p. of 128-129°; n_D^{20} 1.4102; d_4^{20} 0.8200; MR_D 26.64; $C_5H_{11}OH$. Computed 26.93. The figures given in the literature for 2-methylbutanol are [10]: b.p. 129.4°; n_D^{20} 1.4106; d_4^{20} 0.8186. The alcohol does not decolorize a solution of bromine in methanol.

0.0617 g substance: 17.9 ml CH_4 (30°, 753 mm). Found %: OH 19.6. $C_5H_{11}OH$. Computed %: OH 19.3.

The phenylurethane was prepared in the usual manner: m.p. 28-29°. The m.p. given in the literature for the phenylurethane of 2-methylbutanol is 31° [13].

Identification of 2-ethylpropenol. Fractions 11, 12, and 13 were analyzed, the same results being obtained in each case.

3.8 g of the fraction was dissolved in 80 ml of 0.1 N sulfuric acid and boiled for 30 minutes with a reflux condenser. The product had an aldehyde odor. 6 ml of liquid was distilled from the reaction product, 2 ml of which was an oil layer. The dimedon derivative of the oil layer was prepared: square lamellae with a m.p. of 134.5-135.5° after recrystallization from 50% alcohol (m.p. of anhydride 150.5-151°), as was the 2,4-dinitrophenylhydrazone: yellow orthogonal, nearly square lamellae, with a m.p. of 128.2° after recrystallization from alcohol. A test sample mixed with the 2,4-dinitrophenylhydrazone of 2-methylbutanal synthesized via an organomagnesium compound (vide infra) had a m.p. of 128-128.8.

Fraction 13, b.p. 133-133.5°; n_D^{20} 1.4334; d_4^{20} 0.8556. The constants of this fraction were closest of all to those of 2-ethylpropenol, for which Kondakov [11] gives: b.p. 133-134.5°; sp. gr. at 18°, 0.8682.

0.1914 g substance: 8.10 ml of a bromide-bromate mixture (1 ml equivalent to 39.31 mg Br). Found: bromine number 1663 mg Br/g. $C_5H_{10}O$. Computed: bromine No. 1858 mg 1858 mg Br/g. 0.0937 g substance: 27.9 ml CH_4 (31°, 753 mm). Found % O 20.2. C_5H_9OH. Calcd. % OH 1.98. The phenylurethane, prepared in the usual manner, had a m.p. of 49.9-50.3°. 0.1842 g substance: 0.01512 g NH_3 (Kjeldahl). Found %: N 6.75. $C_{12}H_{15}O_2N$. Computed %: N 6.83.

Hydrogenation of Fraction 11. 2.92 g of the fraction and 1.5 g of a Raga catalyst slurry (made with ethyl alcohol) were shaken up together in a Skita apparatus. Hydrogenation lasted 9 hours, 580 ml of hydrogen (20°, 755 mm) being added. The product was filtered and distilled, the bulk of the product distilling at 128-129° and having d_4^{20} 0.820 and n_D^{20} 1.4106.

Synthesis of 2-methylbutanal and its derivatives. 10 ml of absolute ether was poured over 1.5 g of magnesium shavings in a flask fitted with a reflux condenser and a dropping funnel, and a crystal of iodine was added. Then 9.0 g of sec-butyl bromide (b.p. 88.5-90.5°) dissolved in 30 ml of absolute ether was gradually added from the funnel. The flask was first water-cooled and then heated over a water bath. After the reaction was over, 7.7 g of orthoformic ester (b.p. 140-142°) was added and the mixture was boiled for 5 hours. It was allowed to cool, and 40 ml of 6% hydrochloric acid was added to dissolve the precipitate. The oily layer, totalling 5.9 g, was separated in a funnel, charged into a distilling flask containing 35 ml of 15% H_2SO_4, and slowly distilled, the condensate being collected in 15 ml of a 25% bisulfite solution. Agitation caused the bulk of the substance to dissolved; the few drops of oil were removed, and 4 g of sodium bicarbonate was added to the transparent solution, the product being then distilled with steam. The condensate had a strong aldehyde odor (resembling that of butyraldehyde). The 2,4-dinitrophenylhydrazone was prepared from the aqueous solution in the usual manner (nearly square, yellow lamellae, with a m.p. of 128.5-128.8° - from alcohol) as was the dimedon derivative, with a m.p. of 134-134.5° (from 50% alcohol).

Analysis of the aqueous alkaline solution after steam distillation. Acidulation of this solution yielded 43.5 g of formic acid as a weak aqueous distillate that exhibited a HCOOH reaction with $HgCl_2$ as well as with a silver salt. The amount of acid was determined by titration. 60 g of a thick oily liquid with an acid reaction was recovered in addition to the formic acid.

SUMMARY

Reacting formaldehyde with a solution of sodium butylate in butyl alcohol yielded 2-ethylpropenol and its reduction product, 2-methylbutanol-1.

LITERATURE CITED

[1] Yu.A.Gorin, J.Gen.Chem. 16, 238 (1946); 16, 1089 (1946).

[2] M.Ya.Kagan, G.D.Lyubarsky, and O.M.Podurovskaya, Bull. USSR Acad. Sci., 1947, No. 2, 173.

[3] Yu.A.Gorin, J.Gen.Chem. 17, 55 (1947); Yu.A.Gorin, A.A.Vasilyev, and A.K.Panteleeva, J.Gen.Chem. 17, 917 (1947); Yu. A. Gorin and Yu.A.Borgman, J.Gen. Chem. 17, 1286 (1947); Yu.A.Gorin and I.K.Gorn, J.Gen.Chem. 18, 646 (1948); Yu.A.Gorin, J.Gen.Chem. 18, 1065 (1948); Yu.A.Gorin, M.I.Danilina, and N.P. Andreev, J.Gen.Chem. 18, 1069 (1948); Yu.Gorin and K.N.Charskaya, J.Gen.Chem. 18, 1347 (1948).

[4] V.V.Markovnikov and P.V.Zubov, J.Russ.Chem.Soc., 21, 128 (1889).

[5] M.Guerbet, Compte. rend., 128, 511; Ibid., 150, 183

[6] C.Weizmann and associates, J.Chem.Soc., 117, 324 (1920); Chem. and Ind, (London), 56, 587 (1937).

[7] A.P.Terentyev, Bull. Soc. Chim., 35, 1145 (1924); A.P.Terentyev. Memoirs of the Div. of Chem., Assoc. Advancement Nat. Sci., Anthropology, and Ethnography, No. 1. Moscow (1925).

[8] U.S.Patent 1,821,667, 1931; German Patent 527,078, 1931; British Patent 355,208, 1931.

[9] W.Hückel and H.Naab, Ber., 64, 2137 (1931).

[10] A.G.Pukirev, Trans. Inst. Pure Chem. Reagents, No. 18, p. 57. Moscow-Leningrad, (1941).

[11] I.Kondakov, J.Russ.Chem.Soc. 20, 148 (1888).

[12] G.Morgan and Hardy, J.Soc.Chem. Ind., 52, 518 (1933).

[13] W.Marckwald and E.Solda, Ber., 42, 1583 (1909).

[14] A.Haller and F.March, Bull. Soc. chim., 33, 969 (1905).

Received October 2, 1949.

THE FORMATION OF A COORDINATION COMPOUND OF SULFUR TRIOXIDE AND PHENOL

L. I. Kashtanov and L. N. Sokolova

Shilov [1] has advanced the suggestion that in conjugated processes we must expect an unstable compound of the coordination type to be formed between the inductor and the acceptor. Analogous hypotheses might be advanced for the phenomena associated with negative catalysis, where the inhibitor could form an unstable compound with the reaction substance.

The present paper deals with the formation of an unstable coordination compound of the inhibitor phenol and sulfur trioxide.

The retardation of sulfur-trioxide oxidation reactions by phenol has been the topic of papers by Kashtanov and Ryzhov [2] and Kashtanov and Oleshchuk [3], in which it has been shown that phenol, as a surface-active substance, acts chiefly by poisoning the solution surface, thus preventing the start of the sulfur-trioxide oxidation reaction at the phase boundary. The literature contains indirect references to the possibility that sulfur trioxide and phenol form an unstable compound. Garraud's researches [4], for example, indicate the likelihood of the formation of such an unstable compound: when phenol is auto-oxidized in an ammonium sulfite solution containing traces of a copper salt, its ring is sulfonated. Garraud [5] came to a similar conclusion when he introduced sulfo and amino groups into the aromatic ring: he passed air through an aqeuous mixture of hydroquinone, methylamine, and sulfur trioxide containing copper hydroxide as a catalyst and secured a compound in which a sulfite radical and an amino group were both attached to the benzene ring. The only possible explanation for the formation of that compound was oxidation of a coordination compound.

Nevertheless, there is no direct compound of phenol and sulfur trioxide listed in the literature.

EXPERIMENTAL

The experimental conditions were as follows: sulfur trioxide was passed through a chilled saturated solution of phenol. The precipitate was filtered out and dried in a desiccator, and the percentage of sulfur trioxide in the resultant product was determined by titrating the synthesized substance with a 0.1 N solution of iodine. The initial attempts to isolate a coordination compound were made in an aqueous solution of phenol; they met with failure, the coordination compound breaking down as the product was desiccated, and the analysis data yielding fluctuating results. The percentage of SO_2 in the substance isolated varied from 9.4 to 19.5%, for example. Nor did tests with phenol dissolved in benzene, alcohol, or toluene yield the results expected; the precipitate was small, and the resultant coordination compound was so unstable that it was difficult to weigh out a sample of the product. Chilling was done with snow and salt in all the experiments described above.

We resolved to employ deeper chilling and a solution of phenol in chloroform, in which phenol is more readily soluble. We used dry ice for chilling, the temperature of the solution being kept at about -40° during the experiment. An abundant yellowish-green precipitate was thrown down from the chloroform solutions, its crystalline shape differing from that of the phenol. The precipitate was rapidly filtered out while chilled with dry ice and analyzed. The results obtained are listed in the table. To judge by the data in the table the coordination compound should have the formula $(C_6H_5OH)_2SO_2$ (Computed %: SO_2 25.39).

Text No.	Weight of sample, g	% sulfur trioxide
1	1.5962	21.3
2	5.2310	26.9
3	5.6370	24.5
4	2.3864	27.0
5	3.5965	25.7
6	7.6220	21.4
	Average	24.47

The compound was unstable, gradually decomposing when exposed to the air and evolving phenol and sulfur trioxide. When this compound was kept in a desiccator for 3 days, its initial yellowish green color changed to white, its crystalline structure changing from the cubic system to the hexagonal. After 3 days in the desiccator the product exhibited only traces of sulfur trioxide.

We should mention at this point an interesting phenomenon that arose when the sulfur trioxide was passed through the phenol solution. The solubility of the phenol rose markedly, and the solution expanded greatly. This observation was made in all the solutions tested, the volume of the solutions increasing about 1/3. After the solutions had been saturated with sulfur trioxide, samples were taken to determine the percentage of sulfur trioxide in the solution. The mean value of 12 experiments indicates that one molecule (1.07) of sulfur trioxide is absorbed per molecule of phenol.

SUMMARY

1. An unstable coordination compound of phenol and sulfur trioxide has been isolated from a chloroform solution; the compound gradually decomposes in air, giving off phenol and sulfur trioxide.

2. The formula $(C_6H_5OH)_2 \cdot SO_2$ is attributed to the unstable coordination compound of phenol and sulfur trioxide.

LITERATURE CITED

[1] N. A. Shilov, Conjugated Oxidation Reactions, (1905).

[2] Kashtanov and Ryzhov, Bull. All-Union Inst. of Heat Engineering, I, 37, (1935).

[3] Kashtanov and Oleshchuk, J. Gen. Chem. 8, 182, (1938).

[4] Garraud, Bull. Soc. Chim, (V), 1, 1563, (1934).

[5] Garraud, Compt. Rend., 203, 1073, (1936).

Received October 18, 1949.

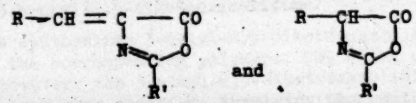
Laboratory of General Chemistry,
S. Ordzhonikidze Institute of
Engineering Economics.

SYNTHESES OF DERIVATIVES OF α-AMINO ACIDS

II. A New Method of Synthesizing Amides of α-Amino Acids

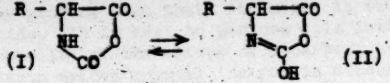
V. F. Kucherov and M. I. Dorochova

Numerous investigations of the reactivity of various azlactones of the subjoined types:

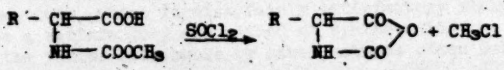


and

have shown that they display a marked trend to enter into many transformations, making it possible to secure various substituted derivatives of the α-amino acids and dipeptides by rupturing the azlactone ring [1]. Derivatives of the 2,5-diketooxazoladines (I) are closely related to the azlactones structurally, provided we presuppose the possible existence of the tautomeric form (II) for these compounds:



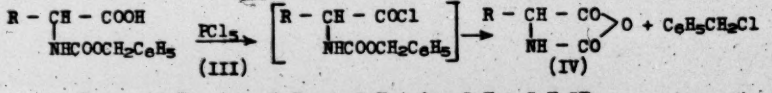
On this assumption we undertook a study of 3-alkyl-2,5-diketooxazolidines with the objective of synthesizing (α-amino) acid derivatives. Notwithstanding the fact that some 3-alkyl-2,5-diketooxazolidines had been described fairly long ago [2], practically no research has been done on their reactivity, apparently because of their instability. In fact these compounds, which are internal anhydrides of N-carboxy alpha amino acids and are usually synthesized by reacting $SOCl_2$ with N-carbomethoxy derivatives of α-amino acids as follows:



split off carbon dioxide extremely readily when exposed to the air or when their solutions are heated, being converted into their polymers. For the same reason some of the 2,5-diketooxazolidines described in the literature have not even been adequately identified, this being especially true of the diketooxazolidines secured as by-products in the decomposition of monoazides of alkyl malonic esters [3].

Our investigations have shown that some 3-alkyl-2,5-diketooxazolidines may be secured and preserved fairly easily when certain conditions are observed for their synthesis and recovery. We synthesized them by reacting carbobenzoxy derivatives of the α-amino acids with PCl_5 in absolute ether, as has been described for the synthesis of some acid chlorides of carbobenzoxy α-amino acids [4]. The initially prepared acid chlorides are able to split off benzyl chloride even when heated to room temperature in ether solution, yielding the

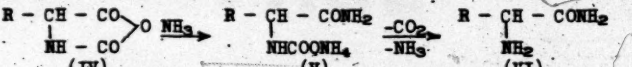
respective 3-alkyl-2,5-diketooxazolidines, which are secured in crystalline form by driving off the ether in vacuum and treating the residue with petroleum ether, and then can be recrystallized from ether. The reaction is as follows:



R = n-C_3H_7; iso-C_3H_7; n-C_4H_9; iso-C_4H_9; $C_6H_5CH_2$.

This reaction, which we have carried out with the carbobenzoxy derivatives of dl-valine, dl-norvaline, dl-leucine, and dl-norleucine, makes it possible to secure yields of 80-90% of the corresponding 3-alkyl-2,5-diketooxazolidines. With carbobenzoxy-dl-phenylalanine, the acid chloride first secured can be recovered in the crystalline state, while boiling it in ether solution yields 80% of crystalline 3-benzyl-2,5-diketooxazolidine.

Heating the synthesized 3-alkyl-2,5-diketooxazolidines converts them quantitatively into the corresponding polymers, CO_2 being split out. Under certain circumstances, however, the 3-alkyl-2,5-diketooxazolidines isolated in the pure state can enter into some reactions involving the rupturing of their oxazoladine ring. Adding diketooxazolidines to a chilled alcoholic solution of ammonia, for example, results in the formation of amorphous precipitates, which have a relatively low decomposition temperature, giving off CO_2 and NH_3 when heated.* When we tried to crystallize these products, they decomposed easily, giving off CO_2 and NH_3 and being converted into the corresponding amides of the α-amino acids (VI), thus definitely proving that their structure is that of ammonium salts of N-carboxy α-amino acids. It is best to perform this last conversion by boiling the isolated ammonium salts of the amides of N-carboxy α-amino acids in benzene, from which the resultant amides crystallize out in adequately pure form upon cooling:



R = n-C_3H_7; iso-C_3H_7; n-C_4H_9; iso-C_4H_9; $C_6H_5CH_2$

These reactions, which furnish fairly satisfactory yields in all their stages, may be a satisfactory new method of synthesizing the amides of the α-amino acids, the yields attainable by other methods often being unsatisfactory.

EXPERIMENTAL

1. Synthesis of Carbobenzoxy-α-Amino Acids (III).

We prepared the carbobenzoxy α-amino acids in the usual manner [4], by condensing 1 mol of the α-amino acid with 1.1 mol of carbobenzoxy chloride in an alkaline solution at 0-3°. After the carbobenzoxy chloride and a corresponding amount of a 1.0 N solution of NaOH had been added, the reaction product was kept at room temperature for 1 hour, then extracted with ether, and the alkaline solution was acidulated with 2.0 N HCl while stirred and chilled to 0°. The precipitated reaction product, which was oily to begin with, gradually hardened and could be recrystallized from CCl_4 to which a small quantity of petroleum ether had been added. When crystallization of the oil formed during acidulation was too slow, it was extracted with ether and desiccated with Na_2SO_4; the ether was driven off in vacuum, the residue being dissolved in a small amount of warm carbon tetrachloride, and petroleum ether being added until the solution turned

* Analysis indicates that their composition is close to that of the ammonium salts of the corresponding amides of N-carboxy α-amino acids (V).

cloudy. This procedure yielded the carbobenzoxy α-amino acids in an adequately pure crystalline form.

a) Carbobenzoxy-dl-valine. 5.8 g of dl-valine yielded 10.5 g of crude carbobenzoxy-dl-valine, with a m.p. of 68-71°. After being recrystallized from carbon tetrachloride to which a small quantity of petroleum ether had been added, the product had a m.p. of 72-73°. Weight: 9.1 g. Yield: 73.3%.

0.1332 g substance: 6.55 ml N_2 (22.5°, 753 mm). Found %: N 5.56.
$C_{13}H_{17}O_4N$. Computed %: N 5.57.

b) Carbobenzoxy-dl-norvaline. 5.8 g of dl-norvaline yielded 9.5 g of carbobenzoxy-dl-norvaline, with a m.p. of 84-86°, the m.p. of which was 86-87° after recrystallization from a mixture of CCl_4 and petroleum ether. Weight: 8.8 g. Yield: 71%.

0.1290 g substance: 6.15 ml N_2 (24.5°, 762.5 mm). Found %: N 5.43
$C_{13}H_{17}O_4N$. Computed %: N 5.57.

c) Carbobenzoxy-dl-leucine. This was synthesized in a similar manner, the yield being 70%. The m.p. of the product was 54-56° after crystallization.

0.1168 g substance: 4.60 ml 0.1 N HCl. Found %: N 5.50
$C_{14}H_{19}O_4N$. Computed %: N 5.28.

d) Carbobenzoxy-dl-norleucine. This was synthesized as above, the yield being 74%. The m.p. of the product was 105-106° after crystallization from a CCl_4 and petroleum ether mixture.

1.1352 g substance: 5.85 ml N_2 (22.5°, 757 mm). Found %: N 4.98.
$C_{14}H_{19}O_4N$. Computed %: N 5.28

II. Synthesis of 3-Alkyl-2,5-diketooxazolidines (IV).

a) 3-Isopropyl-2,5-diketooxazolidine. 8.3 g of finely pulverized PCl_5 was slowly added to a well-stirred solution of 9 g of carbobenzoxy-dl-valine in 40 ml of absolute ether, chilled to a temperature of 3 to 0°. The reaction mixture was stirred for 15 minutes at 0°, and then for one hour at room temperature, after which the solution was filtered to remove the PCl_5 residue, and the ether was driven off in vacuum, without the use of heat, until the mass turned into a syrup or a semi-crystalline mass. 20 ml of petroleum ether was added to the residue, which was re-evaporated in vacuum, resulting in the formation of a crystalline product in the form of needles. Whenever necessary, this operation was repeated several times until a crystalline product insoluble in petroleum ether was fully formed.

The residue was filtered out, thoroughly washed with petroleum ether and with a small quantity of cold absolute ether, and dried in a vacuum desiccator. This yielded 4.6 g of a substance with a decomposition temperature of 79-80°. The yield was 90%. For analysis the product was recrystallized from a small quantity of absolute ether, being recovered as colorless acicular crystals that melted with decomposition at 80-81°.

0.1346 g substance: 11.25 ml N_2 (24.5°, 757.5 mm). Found %: N 9.53.

$C_5H_9O_2N$. Computed %: N 9.77.

3-isopropyl-2,5-diketooxazolidine is readily soluble in the customary organic solvents and is converted with the splitting off of CO_2 into a high-boiling, insoluble polymer with the composition of $(C_5H_9ON)x$ when exposed to the air or when heated.

b) 3-n-propyl-2,5-diketooxazolidine. 4.3 g of crystalline 3-n-2,5-diketooxazolidine, with a temp. decomp. of 65-67°, was secured from 9 g of carbobenzoxy-dl-norvaline by a procedure resembling that employed above. The yield was 84.3%. Needles with a temp. decomp. of 67-69° after crystallization from absolute ether.

0.2488 and 0.1940 g substance: 17.80 and 14.0 ml 0.1 N HCl.
Found %: N 10.02, 10.10. $C_6H_9O_3N$. Computed %: N 9.77.

c) 3-isobutyl-2,5-diketooxazolidine. Like the preceding compound, this was synthesized from carbobenzoxy-dl-leucine, the yield being 80%. The m.p. of the product was 48-50° after crystallization from absolute ether, which conforms to the figure in the literature [5].

d) 3-n-butyl-2,5-diketooxazolidine. This was synthesized by the customary method, the yield being 85%. It was crystallized from absolute ether as acicular crystals with a temp. decomp. of 78-80°.

0.1438 and 0.1308 g substance: 9.35 and 8.60 ml 0.1 N HCl.
Found %: N 9.10, 9.16. $C_7H_{11}O_3N$. Computed %: N 8.93.

e) 3 benzyl-2,5-diketooxazolidine. 5 g of PCl_5 was gradually added, with stirring and chilling to 0°, to a suspension of 6 g of carbobenzoxy-dl-phenylalanine in 40 ml of absolute ether. The solution, which was transparent at first, soon turned into a thick crystalline mass. The reaction product was kept at 0° for 15 minutes and then was diluted with an equal volume of petroleum ether and stirred for 30 minutes at 0°; the precipitate was rapidly filtered out, washed with a small quantity of cold absolute ether, and dried in a vacuum desiccator for 30 minutes. This yielded 4.6 g of a crystalline substance, the acid chloride of carbobenzoxy-dl-phenylalanine. The yield was 72%.

The acid chloride was dissolved in 80 ml of absolute ether, the traces of PCl_5 were filtered out, and the ether solution was boiled over a water bath for one hour. Half of the ether was driven off and 50 ml of petroleum ether was added. The crystalline precipitate was filtered out, washed with a small amount of cold ether, and dried in a desiccator. This yielded 2.5 g of a substance with a temp. decomp. of 119-121°. The yield was 65%, based on the initial carbobenzoxy-dl-phenylalanine. The synthesized 3-benzyl-2,5-diketooxazolidine had a temp. decomp. of 123-125° after crystallization from chloroform, which is the figure given in the literature [5].

III. Synthesis of Amides of α-Amino Acids (VI).

a) dl-norvaline amide. 30 ml of methanol was saturated with NH_3 at 0°, and 3.5 g of 3-n-propyl-2,5-diketooxazolidine was added to the chilled solution. The reaction was energetic, evolving heat and yielding an amorphous white precipitate. After the reaction mixture had been allowed to stand for an hour at room temperature, the precipitate was filtered out, washed with ether, and dried over $CaCl_2$ in a vacuum desiccator. It weighed 3.2 g. The reaction product did not have a sharp decomposition temperature (100-104°); analysis indicated that it was the ammonium salt of N-carboxy-dl-norvaline amide. (V; R = n-C_3H_7).

0.1090 and 0.1006 g substance: 18.40 and 16.75 ml 0.1 N HCl.
Found %: N 23.63, 23.31. $C_6H_{15}O_3N_3$. Computed % N 23.71.

A suspension of 2.9 g of the product in 30 ml of benzene was boiled until all of it dissolved, considerable CO_2 and NH_3 being liberated. The solution was filtered with charcoal, and 10 ml of petroleum ether was added to the filtrate.

The product had a melting point of 67-69° after crystallization from benzene (prisms), and proved to be dl norvaline amide upon analysis. The yield was 1.55 g (60% of the theoretical, based on the original diketooxazolidine).

0.1400 and 0.1708 g substance: 24.02 and 29.05 ml 0.1 N HCl.
Found %: N 24.02, 23.81. $C_5H_{12}ON_2$. Computed %: N 24.12.

b) dl-valine amide. 1.5 g of 3-isopropyl-2,5-diketooxazolidine yielded 1.55 g of an addition product by the same procedure as that employed above; boiling the product in benzene and then crystallizing it yielded 0.75 g of dl-valine amide, with a m.p. of 77-79°. The yield was 61.5%, based on the initial diketooxazolidine.

0.1202 and 0.1100 g substance: 20.68 and 19.0 ml 0.1 N HCl.
Found %: N 24.08, 24.20. $C_5H_{12}ON_2$. Computed %: N 24.12.

The literature [6] gives the m.p. of dl-valine amide as 78-80°.

c) dl-norleucinamide. The preceding method was used to secure 1.45 g of an addition product with a temp. decomp. of 103-107° from 1.5 g of 3-n-butyl-2,5-diketooxazolidine. Analysis of this substance indicated it was the ammonium salt of N-carboxy-dl-norleucinamide. (V; R = n-C_4H_9).

0.1398 and 0.1494 g substance: 21.45 and 22.90 ml 0.1 N HCl.
Found %: N 21.48, 21.46. $C_7H_{17}O_3N_3$. Computed %: N 21.97.

Heating this product in benzene yielded dl-norleucinamide, which had a m.p. of 90-91° after repeated crystallization from benzene. The yield was 65%, based on the initial diketooxazolidine.

d) dl-leucinamide. 1.5 g of an addition product with a temp. decomp. of 95-99° was secured by the preceding method from 1.3 g of 3-isobutyl-2,5-diketooxazolidine; decomposing this product by boiling it in benzene yielded 0.62 g of dl-leucinamide, with a m.p. of 106-108°. The yield was 60%. The literature gives the m.p. of dl-leucinamide as 106-107° [6]. 0.1230 and 0.1318 g sub.: 18.80 and 20.08 ml 0.1 N HCl. Found %: N 21.40, 21.33. $C_6H_{14}ON_2$. Computed %: N 21.52.

e) dl-phenylalaninamide. This was prepared by the foregoing method, the yield being 65%. Lamellae, (from benzene) with a m.p. of 137-139°, which is the figure given in the literature.

SUMMARY

1. A method is described for synthesizing and isolating 3-alkyl-2,5-diketooxazolidines, based on the reaction of carbobenzoxy α-amino acids with PCl_5 in ether.

2. A study has been made of the addition of ammonia to 3-alkyl-2,5-diketooxazolidines, which results in the synthesis of amides of the α-amino acids. A new method is advanced for synthesizing the amides of α-amino acids.

LITERATURE CITED

[1] Organic Reactions, N. J., v. III, 198, (1946).
[2] Leuchs, Ber, 39, 858, (1906).
[3] Th. Curtius, J. prak. chim. 125, 211, (1930).
[4] M. Bergmann, L. Zervas, Ber., 65, 1192, (1932).
[5] Lechs, Geiger, Ber., 41, 1724, (1908).
[6] König, Mylo, Ber., 41, 4435, (1908).

Received October 8, 1949.

SYNTHESES OF DERIVATIVES OF α-AMINO ACIDS

III. The Synthesis of Decarboxydipeptides

V. F. Kucherov and M. I. Dorokhova

A study of the problems involved in the fermentative decarboxylation of peptides and their biochemical transformations led to a chemical and physiological investigation of several decarboxydipeptides, some of which proved to be substances of pharmacological interest [1]. Up to the present time, however, the feasibility of chemical synthesis in this field has been confined to a single known method, involving the condensation of acid chlorides of the α-amino acids with the respective amines, followed by amination, as follows:

$$R-CH(Br)-COCl \xrightarrow{+NH_2Alk} R-CH(Br)-CONHAlk \xrightarrow{NH_3} R-CH(NH_2)-CONHAlk$$

Several decarboxydipeptides [2] and decarboxypolypeptides [3] have been synthesized by this method, and their physiological properties explored. Nonetheless, this method, which furnishes hardly satisfactory yields (especially in the amination stage), is not a satisfactory preparative method for synthesizing the decarboxydipeptides.

In our search for a new method of synthesizing the decarboxydipeptides, we made use of the reactivity of 3-alkyl-2,5-diketooxazolidines, described in our preceding report [4]. We found that, like ammonia, various primary aliphatic amines react readily with 3-alkyl-2,5-diketooxazolidines (I) in alcohol, yielding the corresponding substituted amines of α-amino acids (the decarboxypeptides) (II):

$$\underset{(I)}{R-CH(NH-CO)-CO>O} + AlkNH_2 \rightarrow \underset{(III)}{R-CH(NHCOOH\cdot NH_2Alk)-CONHAlk} \rightarrow \underset{(II)}{R-CH(NH_2)-CONHAlk}$$

In the case of methylamine we were able to recover the intermediate addition products (III) for some of the 3-alkyl-2,5-diketooxazolidines, which yielded the corresponding methylamides of the α-amino acids when heated in alcoholic solution, splitting off carbon dioxide and methylamine (as in the reaction with ammonia).

In the other amines the reaction yields the reaction end product (II) directly. The reaction of the 3-alkyl-2,5-diketooxazolidines with primary amines is extremely smooth, making it possible to secure various decarboxydipeptides with yields of 60-80%. These compounds are high-boiling, viscous liquids, which solidify into low-melting crystalline substances in some cases.

We are pursuing our investigation of the reactive properties of the 3-alkyl-2,5-diketooxazolidines.

EXPERIMENTAL*

General method. One mol of a 3-alkyl-2,5-oxazolidine was gradually added, with stirring and chilling to 13-0°, to a solution of 3-6 mols of the amine in anhydrous methanol. The reaction is rather violent, heat being evolved. The temperature is not allowed to rise above 0°, the transparent solution being kept at this temperature for 30 minutes after all the diketooxazolidine has been added. In the reactions with methylamine the methanol was driven off to dryness in vacuum without the use of heat, the solid amorphous mass that was the intermediate reaction product [the methylamine salt of the corresponding methylamide of the N-carboxy α-amino acid (II)] being filterable after treatment with ether. It was boiled in methanol solution for one hour by way of further processing, the oil left behind when the methanol was driven off being distilled in vacuum. The intermediate reaction products formed with the higher amines cannot be isolated because of their instability and high hygroscopicity. In these instances the transparent methanol solution secured by reacting an excess of the amine with the 3-alkyl-2,5-diketooxazolidine was allowed to stand for one hour at room temperature, after which the methanol and the excess amine were driven off in a slight vacuum, and the residual liquid was distilled in vacuum.

As a rule, the decarboxydipeptides synthesized by this method are pure enough after the first distillation, boiling within a 2° range. The yields are 80-85% for the higher decarboxydipeptides.

1. dl-Valyldecarboxyglycine. 3.3 g of 3-isopropyl-2,5-diketooxazolidine was slowly added, with stirring and chilling to -3-0°, to 20 ml of a 20% solution of methylamine in anhydrous methanol. The solution was kept at 0° for 30 minutes, and then the methanol was driven off to dryness in vacuum without the application of heat. The remaining solid, amorphous reaction product was treated with absolute ether, and the precipitate was filtered out, washed with ether, and dried with $CaCl_2$ in a vacuum desiccator. Weight 3.9 g. The product had a broad temp. decomp. of 96-102°, its analysis indicating that it was the methylamine salt of the methylamide of N-carboxy-dl-valine (III, R = iso-C_3H_7; Alk = CH_3).

0.1112 and 0.1540 g substance: 16.34 and 22.57 ml 0.1 N HCl.
Found % N 20.57, 20.52. $C_8H_{18}O_3N_2$. Computed % N 20.47.

A solution of 3.5 g of the product in 20 ml of methanol was boiled for 1 hour over a water bath, the methanol was driven off, and the residue was distilled in vacuum. This yielded 1.6 g of dl-valyldecarboxyglycine, a bright, viscous liquid with a b.p. of 109-110° at 2 mm. The yield was 53%, based on the initial 3-isopropyl-2,5-diketooxazolidine.

n_D^{20} 1.4712; d_4^{20} 0.9940; MR_D 36.62; Computed 36.94. 0.1444 and 0.1656 g substance: 22.35 and 22.60 ml 0.1 N HCl. Found %: N 21.67, 21.64. $C_6H_{14}ON_2$. Computed %: N 21.52.

2. dl-Norvalyldecarboxyglycine. This was synthesized in the usual fashion from 3-n-propyl-2,5-diketooxazolidine and methylamine without isolating the intermediate reaction product. The yield was 56.5%. A light, viscous liquid with a b.p. of 110-111° at 2 mm.

n_D^{20} 1.4702; d_4^{20} 0.9884; MR_D 36.77; computed 36.94. 0.1604 and 0.1478 g substance: 24.77 and 23.10 ml 0.1 N HCl. Found % N 21.62, 21.88. $C_6H_{14}ON_2$. Computed % N 21.52.

3. dl-Leucyldecarboxyglycine. The method used to synthesize dl-valyldecarboxyglycine was used to secure 2.1 g of the methylamine salt of the methylamide

* The analyses were performed by F. V. Rasina.

of N-carboxy-dl-leucine (III, R = iso-C_4H_9; Alk = CH_3) with a temp. decomp. of 98-104°, from 2 g of 3-isobutyl-2,5-diketooxazolidine and 20 ml of a 20% solution of methylamine in methanol.

1.1260 g substance: 16.85 ml 0.1 N HCl. Found % N 18.72. $C_9H_{21}O_3N_3$. Computed % N 19.16.

Heating this product in methanol, followed by vacuum distillation, yielded 55% of dl-leucyldecarboxyglycine, a thick, colorless liquid with a b.p. of 131° at 3 mm.

n_D^{20} 1.4670; d_4^{20} 0.9690; MR_D 41.30; Computed 41.56.
1.1468 and 0.1814 g substance: 16.95 and 24.70 ml 0.1 N HCl. Found % N 19.11, 19.08. $C_7H_{16}ON_2$. Computed % N 19.42.

The b.p. given in the literature for dl-leucyldecarboxyglycine is 146-147° at 12.5 mm.

4. dl-Norleucyldecarboxyglycine. This was synthesized in the usual manner from 3-n butyl-2,5-diketooxazolidine and methylamine without isolating the intermediate reaction product. The yield was 60%. A bright, viscous liquid with a b.p. of 120-121° at 2 mm.

n_D^{20} 1.4685; d_4^{20} 0.9674; MR_D 41.47; computed 41.56.
0.1652 and 0.1840 g substance: 23.00 and 25.75 ml 0.1 N HCl. Found % N 19.50, 19.61. $C_7H_{16}ON_2$. Computed % N 19.42

The product gradually solidified into an acicular low-melting mass when allowed to stand for a long time.

5. dl-Phenylalanyldecarboxyglycine. This was synthesized in the usual manner from 3-benzyl-2,5-diketooxazolidine and methylamine, the yield being 45%. A bright, viscous liquid, with a b.p. of 165-167° at 3 mm, which solidified into a low-melting acicular mass upon standing.

0.1162 and 0.1212 g substance: 13.15 and 13.55 ml 0.1 N HCl. Found % N 15.48, 15.32: $C_{10}H_{14}ON_2$. Computed % N. 15.71.

6. dl-Valyldecarboxyleucine. 3.6 g (80% of the theoretical) of dl-valyldecarboxyleucine, a viscous, colorless liquid with a b.p. of 140-142° at 5 mm, was synthesized by the general method from 3.5 g of 3-isopropyl-2,5-diketooxazolidine and 6 g of methylamine.

n_D^{20} 1.4620, d_4^{20} 0.9273, MR_D 55.23, computed 55.42.
0.1578 and 0.1804 g substance: 17.22 and 19.48 ml 0.1 N H_2SO_4. Found % 15.28, 15.12. $C_{10}H_{22}ON_2$. Computed % N 15.04

7. dl-Leucyldecarboxyleucine. This was synthesized by the general method from 3-isobutyl-2,5-diketooxazolidine and isoamylamine, the yield being 84.3%. A viscous, colorless liquid with a b.p. of 150-151° at 5 mm.

n_D^{20} 1.4608, d_4^{20} 0.9161, MR_D 59.98, computed 60.03.
0.1858 and 0.1550 g substance, 18.76 and 15.84 ml 0.1 N H_2SO_4. Found % N 14.14, 14.30. $C_{11}H_{24}ON_2$. Computed % N 13.93.

8. dl-Valyldecarboxyphenylalanine. This was synthesized from 3-isopropyl-2,5-diketooxazolidine and β-phenethylamine, the yield being 85%. A viscous, colorless liquid with a b.p. of 190-191° at 5 mm.

n_D^{20} 1.5275, d_4^{20} 1.0376, MR_D 65.33, computed 65.67.
0.1976 and 0.2154 g substance; 18.02 and 19.57 ml 0.1 N H_2SO_4. Found % N 12.77 12.72. $C_{13}H_{20}ON_2$. Computed % N 12.72.

9. dl-Leucyldecarboxyphenylalanine. From 3-isobutyl-2,5-diketooxazolidine and β-phenethylamine, the yield being 85%. A viscous, colorless liquid with a b.p. of 170-171° at 1 mm.

n_D^{20} 1.5212, d_4^{20} 1.0175, MR_D 70.15, computed 70.29.

0.1332 and 0.1824 g substance: 11.55 and 15.73 ml 0.1 N H_2SO_4. Found % N 12.14, 12.07. $C_{14}H_{22}ON_2$. Computed % N 11.96.

The hydrochloride had a m.p. of 202-203°, which is in conformity with the figure given in the literature[2].

10. dl-Norleucyldecarboxyphenylalanine. This was secured, with a yield of 82%, from 3-n-butyl-2,5-diketooxazolidine and β-phenethylamine. A viscous, colorless liquid with a b.p. of 175-176° at 1 mm. Upon standing, the product crystallized rather rapidly into a colorless acicular mass.

0.1996 and 0.1966 g substance: 17.23 and 16.82 ml 0.1 N H_2SO_4. Found % N 12.09, 11.98. $C_{14}H_{22}ON_2$. Computed % N 11.96.

SUMMARY

1. A new method is described for synthesizing decarboxydipeptides, based upon the reaction of 3-alkyl-2,5-diketooxazolidines with primary aliphatic amines.

2. Several new decarbozydipeptides have been synthesized and described.

LITERATURE CITED

[1] Gugenheim, Biochem.Z., 51, 369, (1913).

[2] J.V. Braun, W. Münch, Ber., 60, 345, (1927).

[3] J.V. Braun, A. Bahn, W. Münch, Ber., 62, 2766, (1929).

[4] V. Kucherov and M. Dorokhova, J. Gen. Chem. 21, 1486, (1951).*

Received October 8, 1949.

* C.B. Translation p. 1621.

THE CONDENSATION OF ALKYL VINYL ETHERS WITH WITH AMIDES OF MONOCARBOXYLIC ACIDS

A NEW METHOD OF SYNTHESIZING ETHYLIDENEDIACYLAMIDES

M. G. Voronkov

We have previously explored the addition of monocarboxylic acids to alkyl vinyl ethers, which result in the smooth formation of alkoxy ethylidene carboxylic ethers [1,2] as follows:

$$CH_2 = CH - OAlk + HOCOR \xrightarrow{H^+} CH_3 - CH(OAlk)(OCOR)$$

In the light of this reaction one might expect that amides of monocarboxylic acids would similarly be added in their tautomeric form to alkyl vinyl ethers:

$$CH_2 = CH - OAlk + HOC(R)=NH \xrightarrow{H^+} CH_3 - CH(OAlk)(OC(R)=NH)$$

When the alkyl vinyl ethers were reacted with the acid amides, however, we found that the end products were not alkoxyethylidene-O-acylamides, but ethylidene-di-O-acylamides, together with the corresponding acetal and alcohol, formed as follows:

$$CH_2 = CH - OAlk + HOC(R)=NH \xrightarrow{H^+} \left[CH_3 - CH(OAlk)(OC(R)=NH)\right] \xrightarrow{+HOC(=NH)R}$$

$$\longrightarrow CH_3 - CH(OC(R)=NH)_2 + AlkOH$$

$$CH_2 = CH - OAlk + AlkOH \longrightarrow CH_3 - CH(OAlk)_2.$$

Though the alkoxyethylidene-O-acylamides, which were the hypothetical intermediate reaction products, were not isolated, the foregoing reaction seems to be the most probable one. Nor can we exclude the possibility, moreover, that the alkoxyethylidene-O-acylamide is simultaneously rearranged into the corresponding acetal and ethylidene-di-O-acylamide:

$$2CH_3 - CH(OAlk)(OC(R)=NH) \longrightarrow CH_3CH(OAlk)_2 + CH_3-CH(OC(R)=NH)_2$$

We condensed alkyl vinyl ethers with amides of monocarboxylic acids, using ethyl vinyl and butyl vinyl ethers and acetamide, benzamide, and phenylacetamine. Inasmuch as these amides are not soluble in alkyl vinyl ethers, they were dissolved in hot anhydrous acetone before being placed in reaction.*

A few drops of concentrated hydrochloric acid were added to the reaction mixture as a catalyst. Two to three minutes of heating were sufficient to complete the reaction. The resultant ethylidenediacylamide settled out as a finely crystalline, white precipitate when the reaction mixture was chilled. The yields were 75-85%

We have likewise demonstrated that the formation reaction of ethylidinediacylamide occurs in the absence of a catalyst. Thus, ethylideneacylamide is formed by protracted heating of butyl vinyl ethers and acetamide in a sealed tube at 100°.

Up to the present time, the ethylidenediacylamides have been synthesized by condensing acetaldehyde with acid amides [3,8]** or with nitroles (in sulfuric acid) [7,8]. Ethylidenedibenzamide was likewise prepared by reacting aldehyde ammonia with benzoyl chloride [9]. These compounds were assigned the structure of ethylidenedi-N-acylamides:

$$CH_3 — CH(NHCOR)_2.$$

It seems to us, however, that the structure of O-derivatives $CH_3CH(OC(=NH)R)_2$ is more likely for them, inasmuch as the ethylidenediacylamides are readily hydrolyzed by dilute mineral acids or even by water, yielding acetaldehyde and an amide, then being converted into the ammonium salt of the corresponding acid, and finally ending up as the free carboxylic acid as the result of the action of an excess of the mineral acid. Hence, the hydrolysis reaction, which takes place as follows:

$$CH_3-CH(OC(=NH)R)_2 \xrightarrow{+2H_2O} CH_3CH(OH)_2 + HOC(=NH)R \xrightarrow[H^+]{+H_2O}$$

$$\longrightarrow CH_3CHO + 2RCOONH_4,$$

supports the proposed structure of the ethylidenediacylamides, since we know that O-substituted acid amides (imino ethers) are hydrolyzed similarly:

$$CH_3-\underset{\underset{NH}{\|}}{C}-OR \xrightarrow{+H_2O} CH_3-\underset{\underset{NH}{\|}}{C}-OH + HOR \xrightarrow[H^+]{+H_2O} CH_3COONH_4 + ROH.$$

The N-substituted acid amides, on the other hand, yield amines and carboxylic acids upon hydrolysis:

$$CH_3-\underset{\underset{O}{\|}}{C}-NHR \xrightarrow[H^+]{+H_2O} CH_3-\underset{\underset{O}{\|}}{C}-OH + H_2NR.$$

---

* The presence of water interferes with the reaction.

** The Russian scientist Tavildarov was the first to carry out this reaction, [9].

EXPERIMENTAL

The original alkyl vinyl ethers were prepared and purified by the method described by us previously [2,10] and had the following constants: ethyl vinyl ether – b.p. 35.7° (758.5 mm); d_4^{20} 0.7531, n_D^{20} 1.37657; and butyl vinyl ether – b.p. 93.8° (760 mm); d_4^{20} 0.7792, n_D^{20} 1.40166.

The acetamide was recrystallized from anhydrous acetone, washed with absolute ether and desiccated in vacuum with P_2O_5. M.p. 82.2°.

The benzamide was purified by the same method. M.p. 128.5°.

The phenylacetamide was synthesized by agitating methyl phenylacetate with five times its volume of concentrated ammonia for a long time. The ester in turn was prepared with a yield of 88% by boiling phenylacetic acid with a three-fold excess of absolute methanol in the presence of sulfuric acid; its b.p. was 214° (uncorrected). The crystals of phenylacetamide that settled out were suction-filtered, washed with ammonia and with water, and desiccated in vacuum with H_2SO_4. The yield of the amide, with a m.p. of 157.5°, was 90% of the theoretical. The amide was recrystallized from alcohol, washed with absolute ether, and desiccated in vacuum with P_2O_5.

The acetone was desiccated for 10 days with calcium chloride and distilled into a rectifying tower. Its b.p. was 56.2° (759 mm).

Ethylidenedi-O-acetamide, $CH_3-CH(OC-CH_3)_2$ (NH)

a) Reaction of acetamide with ethyl vinyl ether. 5.9 g (0.1 mol) of acetamide and 15 ml of acetone were placed in a small wide-necked, round-bottomed flask fitted with a reflux condenser. The mixture was heated until all the amide dissolved, and 7.2 g (0.1 mol) of ethyl vinyl ether was added, with constant stirring, following by 2 drops of concentrated HCl. The reaction mixture was heated for another 2-3 minutes and set aside to stand overnight. As it cooled off, a white, finely crystalline precipitate of ethylidenediacetamide began to settle out of the mixture rapidly. The crystals were suction-filtered out, washed with 5 ml of cold absolute ether, and desiccated in vacuum. This yielded 5.9 g (82% of the theoretical) of a substance with a m.p. of 178-179°. One recrystallization from absolute methanol proved to be sufficient to yield a wholly pure ethylidenediacetamide, with a m.p. of 180.5 ± 0.5°.

0.0306 g substance: 5.2 ml N_2 (22°, 765.8 mm); 0.0448 g substance: 7.7 ml N_2 (22.2°, 766.0 mm), 0.0944 g substance: 10.02 g phenol: Δt 0.48°; 0.1260 g substance; 10.2 g phenol: Δ t 0.64°. Found % N 19.43, 19.51. M 138, 141. $C_6H_{12}O_2N_2$. Computed % N 19.43; M 144.17.

A sample mixed with ethylidenediacetamide prepared from acetaldehyde and acetamide [4] exhibited no depression.

The figure given in the literature for ethylidenediacetamide: Noyes and Forman [4] – m.p. 180°.

The synthesized ethylidenediacetamide consisted of colorless prismatic crystals that were insoluble in benzene or ether, but were soluble in alcohol and water. Hydrolysis with dilute sulfuric acid yielded acetaldehyde, acetic acid, and ammonium sulfate. Ethyl alcohol, diethyl acetal, and a small amount of additional ethylidenediacetamide were recovered and identified from the filtered acetone solution and the wash ether after they had been neutralized.

The specified conditions for synthesizing ethylidenediacetamide from ethyl

vinyl ether are the optimum ones. We also ran 12 tests on the condensation of 0.1 mol of acetamide with ethyl vinyl ether in acetone, the quantity of ethyl vinyl ether used varying from 0.05 to 0.2 mol, and that of the acetone ranging from 5 to 25 ml. Varying the amount of solvent within the foregoing range had practically no effect upon the yield of ethylidenediacetamide, whereas reducing the amount of the initial ethyl vinyl ether used to 0.05 mol lowered the yield to 4.2-4.4 g, and raising it to 0.2 mol caused hardly any increase in the yield.

b) Reaction of acetamide with butyl vinyl ether. 30.0 g (0.3 mol) of butyl vinyl ether was added to a hot solution of 17.7 g (0.3 mol) of acetamide in 40 ml of acetone, after which 2 drops of concentrated hydrochloric acid was added with constant stirring. The reaction mass was boiled for a few minutes and then set aside to stand overnight. (As soon as it cooled, it hardened into a snow-white crystalline mass). The crystals were suction-filtered out, washed with absolute ether, recrystallized from methanol, and dried at 100°. The yield of the pure substance with a m.p. of 180.5° was 16.0 g (74% of the theoretical). Samples mixed with the ethylidenediacetamides prepared from ethyl vinyl as well as from acetaldehyde exhibited no depression.

Distillation in vacuum of the neutralized filtrate yielded butyl alcohol, dibutyl acetal, and some ethylidenediacetamide, all of which were identified.

c) Reaction of butyl vinyl ether with acetamide with no catalyst present. 2.96 g (0.05 mol) of acetamide was heated in a sealed tube to 100° with 5.01 g (0.05 mol) of butyl vinyl ether for 50 hours. As the contents of the tube cooled, they crystallized completely. Double recrystallization from alcohol yielded crystals with a m.p. of 180°, which were proved to be the same as ethylidenediacetamide by a mixed fusion test.

Ethylidenedi-O-benzamide $CH_3 - CH(OC(=NH) - C_6H_5)_2$

a) Reaction of benzamide with ethyl vinyl ether. 12.1 g (0.1 mol) of benzamide, 7.2 g (0.1 mol) of ethyl vinyl ether, and 30 ml of acetone were placed in a small wide-necked, round-bottomed flask fitted with a reflux condenser. The reaction mixture was heated until all the benzamide had dissolved, and then 3 drops of concentrated hydrochloric acid were added to the vigorously stirred solution. After being boiled for 2-3 minutes, the reaction mixture was allowed to stand overnight, hardening into a white, finely crystalline mass as it cooled. The crystals were diluted with absolute ether chilled to 0°, and then suction-filtered out, washed with a small quantity of the same solvent, and dried at 100°. The yield of a substance with a m.p. of 196° was 9.4 g (70% of the theoretical). Double recrystallization from alcohol yielded a completely pure substance, small white, silky needles with a m.p. of 204.1 ± 0.5°.

0.0865 g substance: 8.0 ml N_2 (24°, 769.6 mm). 0.0909 g substance: 8.4 ml N_2 (24°, 770 mm). 0.0511 g substance: 10.29 g phenol: Δt 0.14°; 0.0826 g substance; 10.29 g phenol: Δt 0.22°. Found % N 10.46, 10.45. M 256, 260. $C_{16}H_{16}O_2N_2$. Computed % N 10.44, M 268.31.

Figures in the literature for ethylidenedibenzamide: Hepp and Spiess [7] m.p. 204°, Limpricht [8] and Kraut and Schwartz [11] - m.p. 202-204°.

The substance is slightly soluble in hot water, and soluble in chloroform, carbon disulfide, boiling ether, and boiling alcohol. It dissolves readily in concentrated sulfuric and nitric acids, yielding benzoic acid. The latter is also formed when the substance is boiled with 10% sulfuric acid. The substance does not react with a boiling concentrated solution of NaOH. Benzamide and

acetaldehyde are formed when it is heated with water to 150° in a sealed tube of when it is reacted with a 0.1% aqueous-alcoholic solution of HCl.

b) Reaction of benzamide with butyl vinyl ether. 24.2 g (0.2 mol) of benzamide, 20.0 g (0.2 mol) of butyl vinyl ether, and 70 ml of acetone were placed in a small, wide-necked flask fitted with a reflux condenser. The reaction mixture was heated until all the benzamide had dissolved, after which 3 drops of concentrated hydrochloric acid were added to the stirred solution. The reaction mixture was boiled for 2-3 minutes and then set aside to stand overnight. The precipitated crystals of ethylidenedibenzamide were suction-filtered out, washed with a small amount of cold absolute ether, and dried at 100°. The yield was 21.8 g (80% of the theoretical). Double recrystallization from alcohol yielded a substance that fused at 204°. A sample mixed with the ethylidenedibenzamide prepared from the ethyl vinyl ether fused at 203-204°.

Ethylidenedi-O-phenylacetamide $CH_3 - CH(O - \underset{\underset{NH}{\|}}{C} - CH_2C_6H_5)_2$

13.5 g (0.1 mol) of phenylacetamide, 12.0 g (0.12 mol) of butyl vinyl ether, and 90 ml of acetone were placed in a small wide-necked, round-bottomed flask fitted with a reflux condenser. The mixture was heated to boiling (part of the amide remaining undissolved), and 2 drops of concentrated hydrochloric acid were added to it.

The reaction mixture was boiled for five minutes and then set aside to stand overnight, solidifying as it cooled into a finely crystalline mass. The crystals were diluted with 50 ml of acetone, suction-filtered out, washed with the same solvent, and dried at 100°. The yield of ethylidenediphenylacetamide was 12.0 g (81% of the theoretical). A single recrystallization from alcohol yielded a completely pure substance, with a m.p. of 227.3 ± 0.5°, as highly tangled, silky, small white needles.

0.0974 g substance: 8.2 ml N_2 (23°, 770 mm); 0.0996 g substance: 8.5 ml N_2 (26°, 768 mm). 0.0430 g substance 9.55 g phenol: Δ t 0.10°, 0.0764 g substance; 955 g phenol: Δ t 0.19°. Found % N 9.69, 9.52. M 309, 303. $C_{18}H_{20}O_2N_2$. Computed % N 9.45, M 296.96.

Figures in the literature for ethylidenediphenylacetamide: Bernthsen [8] m.p. 227-228°; Henle and Schupp [9] m.p. 224-225°.

The substance is slightly soluble in ether, acetone, or boiling water, dissolving readily in boiling alcohol. Phenylacetic acid and acetaldehyde are formed when it is boiled with 10% H_2SO_4.

SUMMARY

Ethyl vinyl and butyl vinyl ethers and acetamide, benzamide and phenylacetamide have been used to show that alkyl vinyl ethers are readily condensed with the amides of aliphatic, aromatic and aliphatic-aromatic monocarboxylic acids, producing high yields of ethylidenedi-O-acylamides. Ethylidenediacetamide, ethylidenedibenzamide, and ethylidenediphenylacetamide have been synthesized and described, and the structure of these compounds is discussed.

LITERATURE CITED

[1] M.G. Voronkov, Sci. Bull. Leningrad State Univ., No. 19, 12, (1947).

[2] M.G. Voronkov, J. Gen. Chem. 19, 293, (1949).

[3] N. Tavildarov, Jour. Russ. Chem. Soc., 4, 142, (1872).

[4] W. A. Noyes, D. B. Forman, J. Am. Chem. Soc., 55, 3493, (1933).

[5] M. Nencki, Ber., 7, 158, (1874).

[6] A. Bernthsen, Lieb. Ann., 184, 290, (1876).

[7] E. Hepp, G. Spiess, Ber., 9, 1424, (1876).

[8] F. Henle, G. Schupp, Ber., 38, 1369, (1905).

[9] H. Limpricht, Lieb Ann., 99, 119, (1856).

[10] M. G. Voronkov, J. Gen. Chem. 20, 2060, (1950).

[11] K. Kraut, Y. Schwartz, Lieb Ann., 223, 40, (1884).

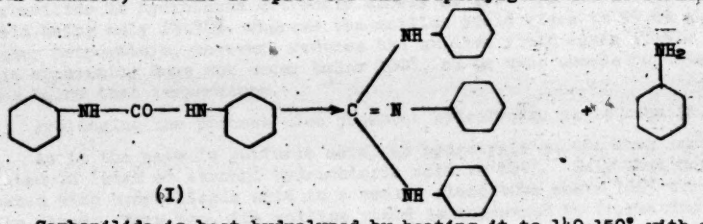
Received September 12, 1949.

Chair of Organic Chemistry
A.A. Zhdanov State University
of Leningrad.

THE HYDROLYSIS OF DIPHENYLUREA (CARBANILIDE)

I. N. Kogan and D. P. Kutepov

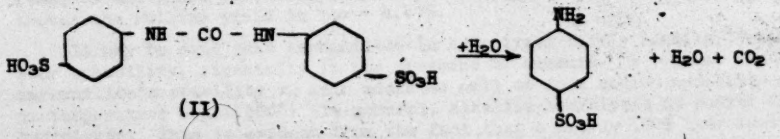
Very little research has been done on the hydrolysis of carbanilide (I). According to the literature, carbanilide is highly stable [1]. Carbanilide was first cleaved successfully into aniline and carbon dioxide by heating it to 180° in a sealed glass tube with concentrated hydrochloric acid [2]. The cleavage products of carbanilide are also secured by boiling it for a long time with acetic anhydride and sodium acetate [3]. When carbanilide is fused with alkalies, aniline is split off and triphenylguanidine is formed [4].



(I)

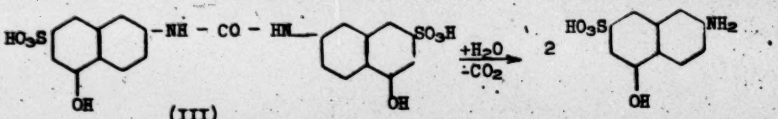
Carbanilide is best hydrolyzed by heating it to 140-150° with an alcoholic solution of ammonia under pressure, yielding aniline and urea [5]. The behavior of carbanilide in a sulfuric acid solution is of interest [6]. Pure carbanilide dissolves in concentrated sulfuric acid even in the cold, forming a pale yellow transparent solution, which can be kept for days without change; dilution with water precipitates the carbanilide anew.

It may be inferred, therefore, that carbanilide forms a sulfate with concentrated sulfuric acid, which is unstable in the presence of water. When carbanilide is dissolved in sulfuric acid and heated over a water bath, we get p,p'-carbanilidedisulfo acid (II), the sulfo derivative being instantly hydrolyzed to yield sulfanilic acid. Carbanilide is apparently hydrolyzed more easily in an alkaline medium, especially if it contains a sulfo group. This is indicated by the paper by Ostrozhinskaya and Kozlova [7], who found that the urea-N-acid (III) was rapidly hydrolyzed in a soda solution, being converted into a salt of an N-acid. The extent of hydrolysis was found to be proportional to the temperature and the length of heating: about 25% of the alic acid was hydrolyzed when heated to 100° in a 3% soda solution for 1 hour.



(II)

* (Alic acid).



(III)

In view of the importance of carbanilide derivatives at the present time we are interested in making a more detailed study of the hydrolysis of carbanilide in various media. Sulfuric-acid hydrolysis was effected by heating the carbanilide with a given concentration of sulfuric acid to 150° in a flask over an oil bath. The amount of aniline, determined by titration with a sodium nitrite solution, increased with a rise in the concentration of the sulfuric acid (99.1% aniline being found when 74.8% sulfuric acid was employed); any further rise in the acid concentration caused the aniline yield to drop off, however, which may be due to the destructive (oxidative) action of highly concentrated sulfuric acid at high temperature (Table 1).

Raising the temperature has about the same effect upon the aniline yield. Carbanilide is hydrolyzed extremely slowly at 100° in 74.8% sulfuric acid, the yield being only 13.78%, whereas the aniline yield rises to 99.6% at 150°. Any higher temperature, however, reduces the aniline yield again (Table 2). Hydrolysis apparently does not occur below 100°, as we were unable to detect any aniline below that temperature.

Prolonging the process also promotes hydrolysis, as is seen in Table 3.

As is the case in sulfuric acid, no hydrolysis occurs when carbanilide is heated in (weak or strong) hydrochloric acid to 100°. Only when carbanilide is heated with hydrochloric acid in a sealed glass tube above 100° does hydrolysis take place. Here too, the aniline yield is increased by increasing the concentration of the hydrochloric acid or by raising the reaction temperature, the aniline yield being 55.95% at 105° and 98.4% at 150° (Table 4). Prolonging the process promotes hydrolysis only up to a certain point, as was the case with sulfuric acid.

Exactly as in acid media, carbanilide is hardly hydrolyzed at all when heated up to 100° with a sodium hydroxide solution, though the aniline yield is 98.8% when it is heated with a 10% sodium hydroxide solution to 150°. When the concentration of the sodium hydroxide is increased, say, to 20%, we find the aniline yield beginning to drop again. Hence, even though increasing the alkali concentration results in an increase of the aniline yield, the destructive effect of a higher reagent concentration is manifested sooner in this case than it was in hydrolysis in an acid medium (Table 5).

As might have been expected from the previously cited data in the literature, ammonia proved to be the most interesting medium for hydrolysis. The carbanilide was hydrolyzed with an aqueous ammonia solution in sealed glass tubes. Heating carbanilide to 150° for 4 hours with a 4.5% ammonia solution yielded an almost theoretical yield (99.25%) of aniline (Table 6). In contrast to all the reagents mentioned previously, hydrolysis takes place in ammonia even at 100°, though the aniline yield is low - 4.47%.

It may be said that carbanilide is hydrolyzed fairly readily, despite its poor solubility, especially in the presence of ammonia. A typical feature is carbanilide's stability in acid media as well as in a sodium hydroxide solution at temperature below 100°. In general, alkaline hydrolysis is easier than acid hydrolysis. This is evident from the fact that a nearly 100% hydrolysis of carbanilide requires the use of very strong hydrochloric acid, with a concentration

of 36%, whereas a concentration of only 10% is required to attain the same percentage hydrolysis with sodium hydroxide. Lastly, when ammonia is employed, its concentration need be only 4.5%. The extraordinary ease of hydrolysis of carbanilide in ammonia is apparently due to the fact that the ammonia reacts with the carbanilide directly, "displacing" aniline and forming urea, which is then decomposed by water into ammonia and carbon dioxide [5].

EXPERIMENTAL

1. Hydrolysis of carbanilide in 56.17% sulfuric acid. 10 g of 56.17% sulfuric acid and 1.050 g (0.005 mol) of carbanilide, with a m.p. of 239°, were placed in a round-bottomed flask fitted with a stirrer, a reflux condenser, and a thermometer. The mixture was heated to 150° for 2 hours 25 minutes, all of the carbanilide dissolving, after which it was poured into ice water. The aniline was determined by diazotization, 18.2 ml of a 0.5N solution of sodium nitrite (K = 1.001) being required. The percentage of aniline was 91.2%.

2. Effect of the concentration of sulfuric acid upon the aniline yield in the hydrolysis of carbanilide in sulfuric acid. Carbanilide and 10 g of sulfuric acid of different concentrations were placed in the flask. The reaction mass was heated to 150° for 1 hour 10 minutes, the subsequent processing being the same as in Experiment 1. The results are listed in Table 1.

TABLE 1

Test No.	Carbanilide, grams	Sulfuric acid concentration	Aniline yield,%
1	1.0532	56.1%	84.3
2	1.0004	64.9	98.1
3	1.0538	74.8	99.1
4	1.0496	85.0	95.1

TABLE 2

Test No.	Carbanilide, grams	Reaction temp, °	Aniline yield,%
1	1.0518	100°	13.78
2	1.0050	125	85.90
3	1.0000	150	99.60
4	1.0020	175	98.38

TABLE 3

Test No.	Carbanilide, grams	Length of hydrolysis hours	Aniline yield, %
1	1.0498	0.5	85.75
2	1.0538	0.75	92.40
3	1.0560	1.0	97.41
4	1.0542	1.25	98.30
5	1.0530	1.5	99.12

3. Effect of temperature upon the aniline yield in the hydrolysis of carbanilide in 74.8% sulfuric acid. The process lasted 1 hour, 10 g of sulfuric acid being employed, The results are listed in Table 2.

4. Effect of the duration of the process upon the aniline yield in the hydrolysis of carbanilide with 10 g of 74.8% sulfuric acid at 150° This test was carried out and the aniline was determined as in the preceding experiment, the results being listed in Table 3.

5. Hydrolysis of carbanilide in 36% hydrochloric acid. 1 g (0.0047 mol) of carbanilide and 20 g of 36% hydrochloric acid were placed in a round-bottomed flask, and the mixture was heated to 100° for 2 hours. In titrating the whole mass after the reaction was over, 0.2 ml of 0.5N sodium nitrite was consumed, so that practically no hydrolysis took place.

6. Hydrolysis of carbanilide in 20% hydrochloric acid at 125°. 20 g of 20% hydrochloric acid and 1.0042 g of carbanilide were placed in a glass tube; the tube was sealed and the contents heated to 125° for 2

hours 30 minutes. The contents of the tube were analyzed in the usual manner, 2.6 ml of 0.5N sodium nitrate being consumed. The aniline yield was 13.76% of the theoretical.

7. Effect of temperature and length of the process upon the hydrolysis of carbanilide in 10 g of 36% hydrochloric acid at 125°. The percentage of aniline was determined by titration. The results are given in Table 4.

TABLE 4

Test No.	Carbanilide in grams	Hydrolysis temp.,	Length of hydrolysis in hours	Aniline yield, in %
1	0.5281	105°	0.5	10.13
2	0.5256	105	1.0	25.80
3	0.5358	105	2.0	55.95
4	0.5000	105	2.5	68.30
5	0.5042	125	0.5	35.10
6	0.5045	125	1.0	56.40
7	0.5267	125	2.0	87.75
8	0.5049	125	2.5	94.83
9	0.5250	150	1.5	86.61
10	0.5021	150	1	94.10
11	0.5150	150	2	98.40
12	0.5000	150	2.5	97.35

8. Hydrolysis of carbanilide in a 5.6% solution of sodium hydroxide at 100°. 1 g of carbanilide and 20 g of a 5.6% sodium hydroxide solution were placed in a round-bottomed flask and the mixture was heated to 100° for 5 hours. When the reaction was over, the mixture was poured into water, acidulated with hydrochloric acid, and diazotized to determine the percentage of aniline, 0.1 ml of 0.5N sodium nitrite being consumed.

9. Hydrolysis of carbanilide in a 19.3% sodium hydroxide solution at 100°. 1.06 g of carbanilide and 8.3 g of a 19.3% sodium solution were placed in a glass tube, the tube was sealed, and the contents were heated to 100° for 6 hours. 1.1 ml of 0.1 N sodium nitrite (K = 1.015) was used. The aniline yield was 1.15%.

10. Hydrolysis of carbanilide in a 10% sodium hydroxide solution at 150°. Except for the reaction temperature, this test was the same as the last one. 19.65 ml of 0.1 N sodium nitrite solution was used. The aniline yield was 99.1%.

11. Effect of temperature and concentration of the sodium hydroxide solution upon the hydrolysis of carbanilide. These tests were made in sealed glass tubes, hydrolysis lasting 4 hours. The results are listed in Table 5.

TABLE 5

Test No.	Carbanilide, in grams	Sodium hydroxide solution, grams	Sodium hydroxide concentration, %	Reaction temp., °	Aniline yield, %
1	1.0508	12	10	100°	1.02
2	1.0420	12	10	125	89.8
3	1.0500	12	10	150	98.0
4	0.5154	10	5.6	150	95.6
5	0.5106	10	10	150	98.8
6	0.5246	10	20	150	97.2

12. Hydrolysis of carbanilide in a 4.5% ammonia solution. 1.05 g (0.005 mol) of carbanilide and 12 g of a 4.5% solution of ammonia were placed in a glass tube, the tube was sealed, and the contents were heated to 150° for 4 hours. The tube contents were then acidulated and diazotized with 0.5N sodium nitrite solution, 19.65 ml of the sodium nitrite solution (K = 1) being

required. The aniline yield was 99.1%.

13. Effect of temperature upon the aniline yield in the hydrolysis of carbanilide in 10 g of 4.5% ammonia for 4 hours. The results of these tests are given in Table 6.

TABLE 6

Test No.	Carbanilide, in grams	Reaction temp., °	Aniline yield, %
1	1.0684	100	4.47
2	1.0402	125	94.15
3	1.0510	150	99.25

SUMMARY

Carbanilide is hydrolyzed in acid as well as alkaline media. It is stable in an acid medium when heated to 100°, and is hydrolyzed to a negligible extent at this temperature in an alkaline medium. The hydrolysis of carbanilide is especially easy in ammonia solutions.

LITERATURE CITED

[1] G. I. Gershon and R.P. Lastovsky, J. Appl. Chem., 9, 2058, (1937).

[2] Rotermund, Lieb. Ann., 175, 262, (1875).

[3] Pechmann, Schmitz, Ber., 31, 3371, (1898).

[4] Hentschel, J. pr. Ch. (2), 27, 502, (1883).

[5] Claus, Ber., 9, 694, 698, (1876).

[6] Hentschel, Ber., 17, 1288, (1884); 18, 977, (1885).

[7] G. I. Ostrozhinskaya and N. A. Kozlova, Aniline Ind. 1932, No. 10, 21.

Received August 30, 1949.

Central Laboratory
M.V. Frunze Chemical Plant
of Dorogomilovo.

THE ACETYLATION OF AROMATIC AMINES WITH ACETYL CHLORIDE IN THE PRESENCE OF SODIUM ACETATE

B. I. Ardashev and E. S. Bych

The commonest method of synthesizing acetylated aromatic amines is heating the amines with acetic acid. This method usually requires considerable time, however, and does not always give satisfactory yields of the acetylated products. Methods have now been developed for acetylating aromatic amines with derivatives of acetic acid: acetylation with acetic anhydride [1] merits consideration; the use of acetamide for this purpose has been described earlier [2]. Gattermann and Wieland's textbook [3] cites the acetylation of aniline with acetyl chloride, half of the aniline not entering into the reaction but forming a hydrochloride.

To make practical use of this method we used the sodium acetate commonly employed in such cases, which reacted to evolve hydrochloric acid, so that practically all of the amine was acetylated. The acetic acid and sodium chloride formed during the reaction dissolve when water is added, the acetyl derivative being thrown down as a precipitate, so that it may be recovered readily. We tested this reaction with 12 different amines, using one mole of acetyl chloride per mole of the moncamine and continuing the reaction for several minutes without the application of heat, inasmuch as the reaction is so energetic as to evolve sufficient heat by itself. It may be used conveniently with minute quantities of an amine, say, for identification purposes. The yields of the acetyl derivatives of the amines are higher than with other acetylation methods, approaching the theoretical in most instances. Inasmuch as the acetylated products are fairly pure and usually do not require further refining, this method may complete successfully with other preparative methods employed in their synthesis.

EXPERIMENTAL

By way of example, we shall describe the acetylation of aniline. 18.6 g of aniline was thoroughly stirred with 8 g of freshly calcined sodium acetate, and 17 g of acetyl chloride was added to the mixture and shaken up with it. The reaction mixture evolved considerable heat and solidified. After it had cooled, about five times its volume of water was added, and the precipitate was filtered out, washed with a small quantity of water, and desiccated. This yielded 26 g of acetanilide as colorless crystals with a m.p. of 114°, or 96% of the theoretical yield.

The results of our acetylation of the several amines used are listed in the table.

No.	Amine	Amount of amine used	Yield of acetyl derivative		Melting point
			Grams	% of theoretical	
1	Aniline	18.6	26	96	114°
2	Orthotoluidine	22	26.6	87	110
3	Paratoluidine	22	29.6	97	147
4	Metatoluidine	22	30	98.5	65
5	Metaxylidine	24.2	29.3	90	128
6	α-Naphthylamine	15	19.2	99	157
7	β-Naphthlyamine	15	19.4	99.7	132
8	Orthoanisidine	25	31.8	95	86
9	Paraanisidine	25	33.5	100	127
10	Metaphenylenediamine	22	33	84	189
11	Paraphenylenediamine	22	35	90	301
12	Benzidine	18.4	26.5	99	317 (caking)

SUMMARY

A study has been made of the acetylation of primary aromatic amines by acetyl chloride in the presence of sodium acetate. Twelve amines have been used to demonstrate that the yields secured with this method are superior to those secured by the other methods known and that it may be recommended for the preparation of pure acetyl derivatives without further crystallization.

LITERATURE CITED

[1] I. S. Ioffe, J. Gen. Chem. 14, 812, (1944).

[2] Werner Kelbe, Ber., 16, 1200, (1883).

[3] L. Gatterman and H. Wieland, Practical Methods of Organic Chemistry, 5th Russ. ed. State Chemical Press (1948).

Received July 25, 1949.

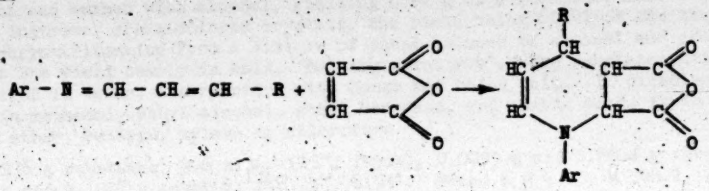
The V. M. Molotov
State University of Rostov

THE REACTION OF SOME ANILS WITH MALEIC ANHYDRIDE

B. I. Ardashev and Z. D. Markova

The diene syntheses of Diels and Adler, effected as we know with all sorts of unsaturated compounds and of extensive practical significance [1] , has not been applied as yet to the products of the reaction of aromatic amines with unsaturated aldehydes, i.e., to diene Schiff bases.

The present research deals with the reaction of maleic anhydride with the following Schiff bases that possess a conjugated double bond: the anil of crotonaldehyde; the anil of cinnamaldehyde; the anils of cinnamic aldehyde and ortho-, meta-, and paratoluidines, metaxylidine, and paraanisidine. We expected this reaction to result in the formation of derivatives of hydrogenated pyridine, as follows:



where R may be an aliphatic or aromatic radical.

In actuality, the resultant anhydrides, possessing a group resembling that of phthalic anhydride, formed indicators of the phenolphthalein and fluorescein type when condensed with the phenols, and quinophthalone dyes when condensed with quinaldine. Moreover, they are quantitatively titrated in alcohol solution with potassium hydroxide and phenolphthalein.

On the other hand, we know that maleic anhydride, which resembles paraquinone structurally, can yield molecule addition products of the quinhydrone type [2]; with dimethylaniline, for example, it forms a colored alloy, the anhydride crystallizing out when the solution is evaporated. This point of view is further confirmed by the fact that, as we have established, ethylidene-p-toluidine and benzalaniline likewise form crystalline products with maleic anhydride.

Inasmuch as all of these products, including the diene anils, are decomposed when heated with alkalies, yielding the initial amines, it must be supposed that they are molecular compounds. They may be employed successfully to identify the anils.

EXPERIMENTAL

Maleic anhydride and crotonylideneaniline. 0.6 g of crotonylideneaniline, prepared by a method described by one of the present authors previously [3] , 0.4 g of maleicanhydride, and 40 ml of xylene were placed in a flask fitted with

a reflux condenser and heated over an oil bath for 3 hours to the temperature of 135-140°, at which they gently boiled. After the mixture had cooled, the xylene was driven off with steam, the solid product remaining in the distilling flask being filtered out of the water and purified by boiling with activated charcoal and alcohol in a flask fitted with a reflux condenser set over a water bath.

After the alcoholic solution had been filtered and diluted with water, the anhydride was precipitated as 0.344 g of minute, sand-colored crystals with a m.p. of 122-124°, representing 34.1% of the theoretical yield. It is insoluble in water or ether, freely soluble in alcohol, acetone, benzene, xylene and chloroform; and soluble when heated in acetic acid. Its molecular weight was determined by the Rast method, with approximate accuracy, since the substance decomposes partially at its melting point.

0.2080 g substance: 10.8 ml N_2(17°, 759 mm) 0.01 g substance: 0.1502 g and 0.1522 g camphor: Δt 11.9°, 11.1°. Found % N 6.06, M 223.8, 236.7. $C_{14}H_{13}O_3N$. Computed % N 5.75, M 243.

Maleic anhydride and cinnamylideneaniline. 0.5 g of the anil of crotonaldehyde, prepared by the method described earlier [4], was heated for 10-15 minutes over a water bath with 0.25 g of maleic anhydride in 20 ml of xylene, after which the mixture was set aside to stand until the following day. The precipitate was filtered out and washed with alcohol, yielding 0.44 g of a substance consisting of minute, lustrous, cream-colored crystals, the yield being 60.2% of the theoretical. Recrystallization from a mixture of equal volumes of alcohol and chloroform cut the yield nearly in half. Melting point 204°. The substance dissolves when boiled in water, its reaction with Congo red being acid. It dissolves when heated in methanol, ethyl alcohol, ethyl benzoate, and acetic acid; it is soluble in ether, benzene, xylene or chloroform.

0.2276 g substance: 9.6 ml N_2 (15°, 755mm), 0.0095 g and 0.0098 g substance, 0.1513 g and 0.1518 g camphor: Δt 8.15°, 8.95°. Found % N 4.93, M 308.1, 288.5. $C_{19}H_{15}O_3N$. Computed % N 4.59, M 305.

Condensation with quinaldine. 0.4 g of the anhydride and 0.12 g of zinc chloride were heated to 170° over an oil bath, 0.25 g of freshly distilled quinaldine was added, and the mixture was heated to 180-190° for 6 hours, in a flask with a reflux condenser, the temperature being raised to 220° for the last 30 minutes. This yielded 0.45 g of dye in the shape of a brown powder with a m. p. of 170°. After the dye had been sulfonated with oleum, it was a dark-brown powder that was soluble in water and dyed silk a chocolate color in an acid bath. It did not fix cotton.

Maleic anhydride and cinnamylidene-p-toluidine. We first synthesized the Schiff base of paratoluidine and cinnamic aldehyde, which is not described in the literature. 1 g of paratoluidine and 1.24 g of freshly distilled cinnamic aldehyde were placed in a porcelain dish, and the mixture was heated for 15-20 minutes over a water bath. The resultant solid product was washed with alcohol, the yield being 1.36 g, or 65.8% of the theoretical. Recrystallization from alcohol cut this yield almost in half. Cinnamylidene-p-toluidine consists of shiny light-yellow lamallae with a m.p. of 79°. It is soluble in methanol, ethyl alcohol, ether, chloroform, benzene, xylene, and acetic acid, though insoluble in water. It dissolves in dilute hydrochloric acid, being precipitated from the solution when the latter is alkalinized with sodium hydroxide.

0.2220 g substance: 12.8 ml N_2 (23°, 760 mm), 0.01 g substance: 0.15 g camphor: Δt 11.8. Found % N 6.58, M. 225.9. $C_{16}H_{15}N$. Computed % N 6.33, M 221.0.

0.5 g of cinnamylidene-p-toluidine and 0.22 g of maleic anhydride were heated in 20 ml of xylene for 10-15 minutes over a water bath, and the mixture was then allowed to stand until the following day, when the precipitate was filtered out and washed with alcohol. The product yield was 0.42 g, or 58.3% of the theoretical. The yield dropped to 40% of the theoretical after recrystallization from equal volumes of alcohol and chloroform. The addition product consisted of light-yellow, acicular crystals with a m.p. of 185°. It is soluble when heated in methanol, ethyl alcohol, ethyl benzoate, and acetic acid and insoluble in ether, chloroform, benzene, or xylene; it dissolves when boiled in water, giving an acid reaction with Congo red.

0.2136 g substance: 9.2 ml N_2 (20°, 766 mm); 0.1860 g substance: 7.2 ml N_2 (25°, 755 mm); 0.01 g substance; 0.20 g camphor: Δ t 6.4°. Found % N 5.01, 4.37, M 312.5. $C_{20}H_{17}O_3N$. Computed % N 4.38, M 319.

It was found that the reaction of maleic anhydride with a Schiff base also occurs at room temperature.

Maleic anhydride and cinnamylidene-o-toluidine. 1.0 g of cinnamylidene-o-toluidine and 0.45 g of maleic anhydride were dissolved in 15 ml of benzene. The solution was set aside to stand until the following day, when the precipitate was filtered out and desiccated. The yield of the dry product was 0.68 g, or 47.2%, dropping to 0.20 g, or 14% of the theoretical, after recrystallization from alcohol. The addition product consisted of thin, white, fibrous crystals with a m.p. of 120°, soluble in methanol and ethyl alcohol, acetone, chloroform, ethyl acetate, and acetic acid, and very sparingly soluble in ether.

In a similar manner we secured the products of the reaction of maleic anhydride with cinnamylidene-m-toluidine: yellow crystals with a m.p. of 175°; with cinnamylidene-m-xylidene – yellow crystals with a m.p. of 162°; and with cinnamylidene-p-anisidine – yellow crystals with a m.p. of 195°. When these anhydrides were fused with phenol, they formed condensation products that color an alkali red, exactly as does phenolphthalein. Fusing them with resorcinol yields dyes that turn ammonia red-brown in transmitted light and green in reflected light, exactly as does fluorescein.

We subsequently found that maleic anhydride likewise forms crystalline products with the following compounds under analogous conditions: lemon-yellow crystals with a m.p. of 204° when reacted with ethylidene-p-toluidine and minute cream-colored crystals with a m.p. of 209° when reacted with benzalaniline.

None of the products of the reaction of the anils with maleic anhydride synthesized in this research has been described in the literature previously.

SUMMARY

1. It has been found that anils react with maleic anhydride to form crystalline products that are molecular compounds of the quinhydrone type.

2. The reaction of the anils with maleic anhydride may be recommended as a means of identifying the anils.

LITERATURE CITED

[1] B.A. Kazansky, Prog. Chem. 3, 1, 117, (1934).
[2] W. Hückel, Theoretical principles of organic chemistry, Vol. 1, p 104, (1933); V. Shlenk and E. Bergman, Organic Chemistry, p. 613, (1938).
[3] B. I. Ardashev and M. M. Kurbatov, J. Gen. Chem. 16, 53, (1946).
[4] O. Doebner and W. Miller, Ber., 16, 1664, (1883).

Received July 20, 1949. V.M.Molotov State University of Rostov

RESEARCH ON THE SULFONATION REACTION

XVII. Hydrolysis of Sulfo Acids with Hydrochloric, Sulfuric, and Phosphoric Acids

A. A. Spryskov and N. A. Ovsyankina

We know that the hydrolysis of sulfo acids (desulfuration), represented by the equation:

$$RSO_3H + H_2O \rightarrow RH + H_2SO_4,$$

is accelerated greatly in the presence of a mineral acid, as a rule. Only a single exception has been noted to this rule; it was described in our Report XIII [1]. The same paper contains a brief survey of the literature on the hydrolysis of sulfo acids, indicating that numerous research workers secured highly contradictory results in their determinations of the hydrolysis temperature of the same sulfo acids. These discrepancies occurred because the determinations were made under different conditions. The hydrolysis conditions, which include the temperature, the sulfo acid concentration, the nature and concentration of the mineral acid, and the duration of the reaction, all affect the result, i.e., the percentage of the sulfo acid that is decomposed. We have reported previously on the variation of the reaction rate with the composition of the mixture (water, sulfo acid, and mineral acid); in the present paper we have endeavored to compare the hydrolysis reaction rates as affected by the nature of the mineral acid employed (hydrochloric, sulfuric, or phosphoric).

The tests were run by heating α-naphthalenesulfonic acid and sulfosalicylic acid to 100° for 25 hours in sealed tubes in an Eickmann apparatus with various quantities of hydrochloric, sulfuric, or phosphoric acid, always with 4.5 mols of water present.

The results of our tests with α-naphthalenesulfonic acid, reproduced in Fig. 1, indicate that mineral acids accelerate the hydrolysis reaction in highly different degrees. When no mineral acid is present, 2% of the sulfo acid is hydrolyzed under the conditions specified, the hydrolyzed percentage being much higher in the presence of a mineral acid. Hydrochloric acid is the best accelerator, sulfuric acid coming next, with phosphoric acid the least active of the three.

The concentrations of the various mineral acids at which hydrolysis takes place at the same rate are listed in the table. These figures show that the concentration of the sulfuric acid has to be 2 to 2.3 times as high as that of the hydrochloric acid for hydrolysis to take place at the same rate, while the phosphoric acid concentration has to be 3-4 times as high as the hydrochloric acid concentration for the same hydrolysis rate. The figures given in the table indicate that this difference (this ratio) gradually diminishes as the concentration of the mineral acid is increased.

The results of our experiments using sulfosalicylic acid, given in Fig. 2, show that hydrolysis is greatly accelerated by hydrochloric and sulfuric acids here, too, while phosphoric acid exerts a very slight accelerating effect upon the reaction.

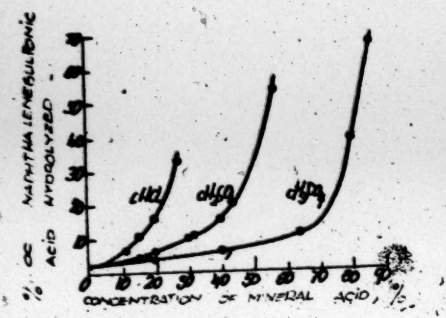


Fig. 1.

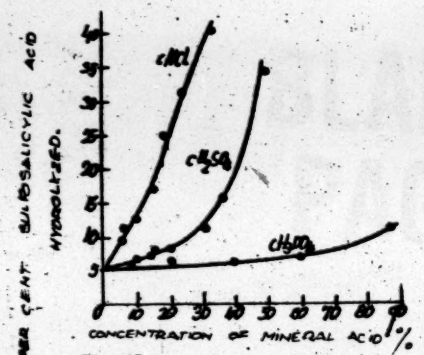


Fig. 2.

When no mineral acid is used, 5.2% of the sulfosalicylic acid is hydrolyzed under the conditinns specified above, the hydrolysis of the sulfosalicylic acid totaling 6-7% when 8 to 60% of phosphoric acid is present; only at a phosphoric acid concentration of 87% is the per cent hydrolysis twice as high as it is in water. As was the case with α-naphthalenesulfonic acid, hydrochloric acid accelerates the rate of hydrolysis more than does sulfuric acid. The table also gives the concentration of the several mineral acids for which sulfosalicylic acid is hydrolyzed at the same rate. For hydrolysis to occur at the same rate, the concentration of sulfuric acid must be 3-4 times as high as that of the hydrochloric acid at low concentrations, and about twice as high at higher concentrations of these mineral acids. 80% phosphoric acid hydrolizes at the same rate as 6.5% hydrochloric acid, i.e., its required concentration is 12 times as high.

Hence, the experimental data cited by various authors on the hydrolysis temperature for sulfo acids are incommensurable for various reasons, especially because the determinations were made with different mineral acids in many cases. Veseli and Stoyanova [2] ran their tests to determine the hydrolysis temperature of sulfo acids using phosphoric acid. That is probably the main reason why their data give the hydrolysis temperature of benzenesulfonic acid as 227°, while Ipatyev and Petrov [3] who ran their tests with sulfuric acid, give it as 170°. Similarly, Veseli and Stoyanova give the hydrolysis temperature as 137° for metaxylolsulfonic acid, while Ipatyev and Petrov give 122°. The figure given by Kizhner for orthoxylenesulfonic acid [4] likewise differs from that given by Veseli and Stoyanova.

As far back as 1901 Crafts [5] advanced the hypothesis that only the dissociated molecule of the sulfo acid underwent hydrolysis and that mineral acids were not catalysts in the ordinary sense of the term, but were agents that suppressed the dissociation of the sulfo acid. This assertion appears to be quite probable and has, therefore, been supported by many researchers. It cannot, however, explain the fact that the hydrolysis of chlorobenzenesulfonic acid [1] is not accelerated in the presence of mineral acids. Moreover, it seems to us premature to deny a purely catalytic influence of the mineral acid anion, inasmuch as Crafts did not have adequate experimental data available on which to base such an assertion.

British chemists have recently asserted that the rate of desulfuration does

not depend upon the concentration of the sulfo acid or the nature of the inorganic anion. This conclusion was not supported by published experimental data, and we reject it as contradicted not only by our own observations.

Concentrations of Mineral Acids at which Hydrolysis Occurs at the Same Rate

Sulfo Acid	Sulfo Acid Hydrolyzed %	Mineral Acid Concentration: Hydrochloric acid	Sulfuric acid	Phosphoric acid	Ratios (concent.) H_2SO_4 / HCl	H_3PO_4 / HCl
α-Naphthalenesulfonic acid	4	6	14	25	2.3	4.2
	7	11	24	47	2.2	4.3
	10	14.5	31	61	2.1	4.2
	15	19	39	70	2.0	3.7
	25	24.5	47	76	1.9	3.1
	35	27	52	80	1.9	3.0
Sulfosalicylic acid	10	6.5	26	80	4.0	12
	15	12	36		3.0	
	20	17	41		2.4	
	25	21	44		2.1	
	35	27	50		1.0	

EXPERIMENTAL

Pure 5-sulfosalicylic acid was prepared by heating 80 g of salicylic acid for 6 hours with 200 g of 95% sulfuric acid. The sulfo mixture was poured into 1 liter of water, and the excess sulfuric acid was neutralized with barium carbonate. The precipitated barium carbonate was squeezed out, and the filtrate was evaporated over a water bath until its volume was about 200 ml. The crystallizing sulfo acid was filtered out and recrystallized from 20% hydrochloric acid. This yielded 70 g of a product that contained 1 molecule of crystallization water after having been dried at 70° and had a molecular weight of 236.5--237.1 according to titration with 0.1 N alkali (236.2 is called for theoretically). Dehydrating the substance by heating it in capillaries to 120-130° yielded a product with a m.p. of 219.5 - 221°.* The preparation of the pure α-naphthalenesulfonic acid has been described earlier.

The tests of the hydrolysis reaction were run as follows: A sample of the sulfo acid weighing 0.5 to 1 g was heated in a sealed tube with a given quantity of water and the mineral acid in an Eickmann apparatus. The percentage of the sulfo acid that was hydrolyzed was calculated from the amount of sulfuric acid formed, as determined gravimetrically in the form of barium sulfate. In some tests, run with sulfuric acid, the degree of hydrolysis was determined by the increase of acidity volumetrically, i.e., by titration with a 0.1 N solution of sodium hydroxide.

SUMMARY

It has been found that mineral acids accelerate the hydrolysis of α-naphthalenesulfonic acid and of 5-sulfosalicylic acid in varying degree. Hydrochloric acid accelerates hydrolysis most, sulfuric acid next, and phosphoric acid least. Phosphoric acid produces hardly any acceleration of the hydrolysis of 5-sulfosalicylic acid in concentrations up to 60%.

* E. Fischer found the m.p. of anhydrous sulfosalicylic acid to be about 224° [6].

LITERATURE CITED

[1] A. A. Spryskov and N. A. Ovsyankina, J. Gen. Chem. 20, 1043, (1950). *

[2] V. Vesely and Stoyanova, Collection Czechoslav. Chem. Communications, 9, 465, (1937); Chem.Zentr., I, 581, (1938).

[3] V. N. Ipatyev and A. Petrov, Ber., 59, 1737, (1926).

[4] H. M. Kizhner, J. Gen. Chem. 3, 578, (1933).

[5] J. M. Krafts, Ber., 34, 1350, (1901).

[6] R. Fischer, Pharm. Z., 81, 243, (1936); Chem. Zentr. I, 4761, (1936).

Received October 13, 1949.

Ivanovo Institute of Chemical Technology

and

Ivanovo State Institute of Medicine.

* See C.B. Translation, p. 1083.

SOME DERIVATIVES OF 2-NAPHTHOL-4-SULFONIC ACID

II. Sulfonation of 2-Naphthol-4-sulfonic Acid

S. V. Bogdanov and I. B. Migacheva

In 2-naphthol itself, as well as in its derivatives that can be sulfonated by sulfite in the presence of an oxidizing agent (including 2-naphthol-4-sulfonic acid), substitution takes place only at the 1 position in this process [1]. Substitution of this sort is observed, more or less, in 2-naphthol, 2-hydroxy-3-naphthoic acid, 2-naphthol-6-sulfonic acid, and 2-naphthol-7-sulfonic acid and also when the customary sulfonating agents, such as sulfuric acid, fuming sulfuric acid, and chlorosulfonic acid, are employed [2]. We therefore thought it advisable to ascertain the behavior of 2-naphthol-4-sulfonic acid toward the oxidizing sulfite as well as to other sulfonating agents, the chief of which is fuming sulfuric acid. Experiments have shown that 2-naphthol-1,4-disulfonic acid is not present in the end product of the sulfonation of the sodium salt of 2-naphthol-4-sulfonic acid with an excess of 20% oleum. Comparison of the synthesized disulfo acid with other, more likely isomers: 2-naphthol-4,8-disulfonic acid, and 2-naphthol-4,6-disulfonic acid indicated that 2-naphthol-4,8-disulfonic acid had been produced. This does not disprove, to be sure, the possibility that 2-naphthol-1,4-disulfonic acid is formed at the initial instant of sulfonation, nor that some isomeric naphtholdisulfonic acids are present. The 2-naphthol-4,8-disulfonic acid used in this comparison was secured by decomposing 2-diazonaphthalene-4,8-disulfonic acid, while the 2-naphthol-4,6-disulfonic acid was prepared by reducing 1-diazo-2-naphthol-4,6-disulfonic acid with an alkaline solution of stannous oxide by the procedure described previously [3].

EXPERIMENTAL

Sulfonation of 2-naphthol-4-sulfonic acid. 25 g (about 0.1 mol) of the pure, desiccated sodium salt of 2-naphthol-4-sulfonic acid was added to 75 g of 20% oleum at 4-12° during the course of one hour. Owing to the thickening of the mass, 37 g of 30% oleum was added one hour after the monosulfo acid had been added, and the mixture was allowed to stand for 18 hours at 12-18°, after which it was poured over ice, and the disulfo acid was converted into its sodium salt in the usual manner. Diluted samples of a solution of the sodium salt of the sulfo acid coupled extremely slowly with diazo-p-toluene, m- and p-nitro diazonium, nor did boiling the samples with concentrated sulfuric acid improve their coupling ability. Whereas the coupling products of 2-naphthol-4-sulfonic acid are deeply colored and slightly soluble, all we secured in this case, both before and after acid hydrolysis, were reddish-orange solutions. This indicated the complete absence of the initial 2-naphthol-4-sulfonic acid and of 2-naphthol-1,4-disulfonic acid in the sulfonation product. When the solution of the sodium salt of the sulfo acid was evaporated, a precipitate consisting of four- and six-sided stubby prisms settled out; they were recrystallized from aqueous alcohol

1.1423 g substance: loss in weight (100-120°) 0.1324 g. 0.2719 g dry substance: 0.1095 g Na_2SO_4. Found %: H_2O 11.59: Na 13.05. $C_{10}H_6O_7S_2Na_2 \cdot 2.5H_2O$. Computed %: H_2O 11.45. $C_{10}H_6O_7S_2Na_2$. Computed % Na 13.22.

The substance is readily soluble in water. The solutions are colorless and display faint blue fluorescence, which grows stronger when soda is added. The solution remained colorless when reacted with nitrous acid, while ferric chloride colored it a brilliant blue. Coupling with diazo-m-nitrobenzene yielded a reddish-orange soluble dye, though quantitative coupling took place only in a fairly concentrated solution. Titration of a solution of 0.4038 g of the anhydrous substance and 6 g of soda in 50 ml of water required 23.0 ml of 0.05 N-diazo-m-nitrobenzene, representing 99.2% of the disodium salt of the naphtholsulfonic acid. The solid salt was added during titration in order to precipitate the dye (orange needles).

2-Naphthol-4,8-disulfonic acid. The diazo compound secured from 0.1 mol of 2-naphthylamine-4,8-disulfonic acid was gradually added to 300 ml of boiling 10% sulfuric acid. The liquid was neutralized with chalk and soda, and the filtrate left after the precipitate had been filtered out was evaporated to small volume. The resultant precipitate was recrystallized from water.

2.2800 g substance: loss of weight (120°) 0.2806 g. 0.3139 g dry substance, 0.1261 g Na_2SO_4. Found % H_2O 12.30, Na 13.02. $C_{10}H_6O_7S_2Na_2 \cdot 2.5\ H_2O$. Computed % H_2O 11.45. $C_{10}H_6O_7S_2Na_2$. Computed %: Na 13.22.

Short prisms, readily soluble in water. The fluorescence of the solutions and their behavior with nitrous acid, ferric chloride, and diazo-m-nitrobenzene were the same as for the sulfonation product of 2-naphthol-4-sulfonic acid.

2-Naphthol-4,6-disulfonic acid. The initial 1-amino-2-naphthol-4,6-disulfonic acid was prepared by dissolving 1-nitroso-2-naphthol-6-sulfonic acid in an excess of bisulfite and acidulating the solution with hydrochloric acid, as specified by M. Böniger [4]. The diazo compound secured from 0.12 mol of the disodium salt of 1-amino-2-naphthol-4,6-disulfonic acid and precipitated by barium chloride from a solution acidulated with hydrochloric acid was added to an alkaline solution of 0.18 mol of stannous chloride. When the reaction was over and the barium and tin had been eliminated, the solution was evaporated. The precipitated substance was recrystallized from aqueous alcohol.

1.5470 g substance: loss of weight (125°) 0.2240 g. 0.3500 g dry substance: 0.1392 g $NaSO_4$. Found %: H_2O 14.47, Na 12.88. $C_{10}H_6O_7S_2Na_2 \cdot 3H_2O$. Computed % H_2O 13.44. $C_{10}H_6O_7S_2Na_2$. Computed %: Na 13.22.

Elongated thin flat prisms, readily soluble in water. The solutions display a faint blue fluorescence, changing to violet-blue when soda is added; the they turn dirty blue when ferric chloride is added. They react with diazo-m-nitrobenzene to form a reddish-orange soluble dye: coupling is extremely slow in dilute solutions. Nitrous acid colors dilute solutions yellow. The nitroso compound, prepared in the usual manner, is precipitated by potassium chloride as elongated thin needles.

SUMMARY

Sulfonation of 2-naphthol-4-sulfonic acid with 20% oleum at 3-18° yields 2-naphthol-4,8-disulfonic acid.

When an alkaline solution of stannous oxide is reacted with 1-diazo-2-naphthol-4,6-disulfonic acid, 2-naphthol-4,6-disulfonic acid is formed.

LITERATURE CITED

[1] S. V. Bogdanov, J. Gen. Chem. 9, 1145, (1939) and earlier.

[2] G. Tobias, German Patent 74688, K.D. Shcherbachev, J. Appl. Chem. 8, 1216, (1935); O Dressel, R. Kothe, Ber., 27, 1206, (1894); K. Dziewonski, A. Loewennof, Zbl., II, 45, (1928).

[3] S. V. Bogdanov and I. B. Migacheva, J. Gen. Chem. 19, 1490, (1949).

[4] M. Böniger, Ber., 27, 3050, (1894).

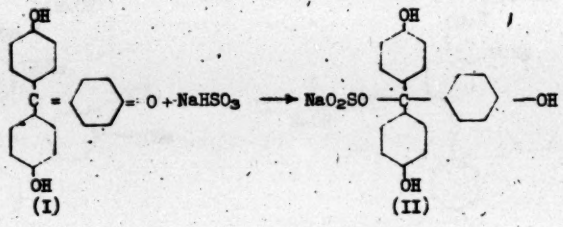
Received October 2, 1949.

The K.E.Vorishilov Organic Intermediates and Dyes Research Institut

XIV. The Structure of Bisulfite Derivatives of Hydroxyfuchsone Dyes

I. S. Joffe

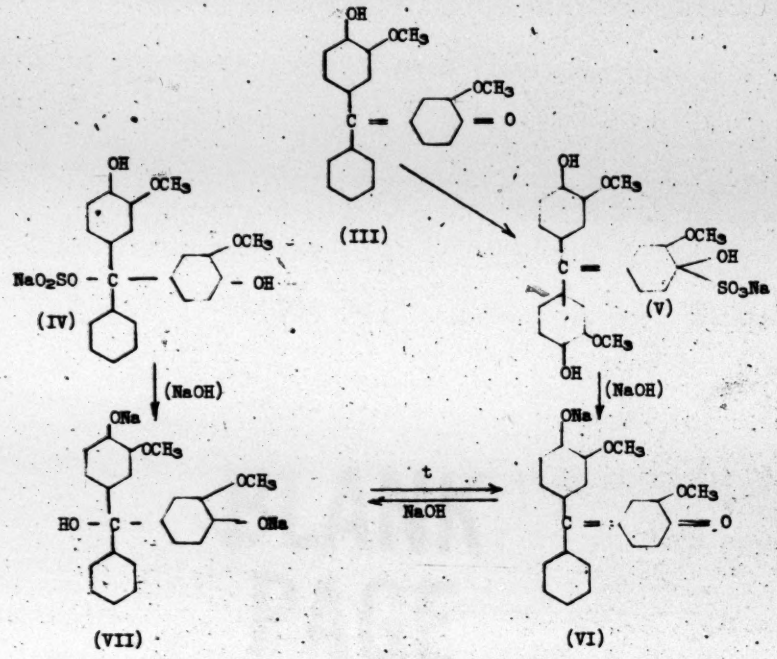
Not enough research has been done on the structure of the bisulfate derivatives of the fuchsones and the hydroxyfuchsone dyes. A. Bayer [1], at the beginning of the century, put forward the hypothesis that the bisulfite derivative of aurin (I) is formed as a result of the addition of bisulfite at the conjugated system of the dye's methylenequinone grouping and constitutes a sulfite salt of the corresponding carbinol derivative of the structure (II).



This hypothesis was not borne out experimentally; it was based solely on the fact that the bisulfite derivatives of the hydroxyfuchsone dyes are colorless and are readily decomposed by mineral acids or alkalies.

Not so long ago [2], on the basis of a more thorough-going study of the properties of the bisulfite derivatives of hydroxyfuchsone dyes, we expressed our doubts concerning the correctness of the structure suggested for these substances by Bayer; we believed it was more likely that the bisulfite derivatives of the hydroxyfuchsone dyes are formed as the result of the interaction of the bisulfite with the dye's carbonyl group and that they are α-hydroxysulfo acids. By now we have secured new and, we believe, convincing proofs of our supposition. These proofs stem from a study of the decomposition of the bisulfite derivatives of hydroxyfuchsone dyes by alkaline agents.

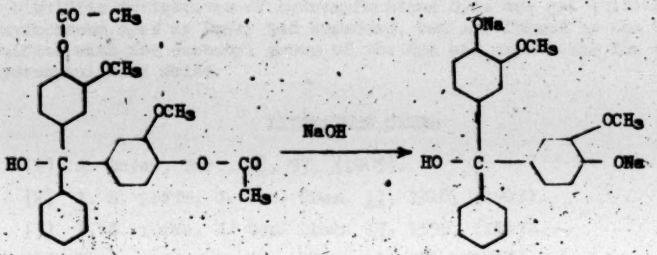
The bisulfite derivative of 3,3'-dimethoxybenzaurin [3] (III) is a very convenient research object in this connection. According to Bayer's notions, this bisulfite derivative should have the structure (IV), whereas we assumed that this substance was an α-hydroxysulfonic acid with the structure (V). Our supposition is based upon the following observations: when any alkaline agent is added to an aqueous solution of the bisulfite derivative, the latter is decomposed almost instantaneously, and the solution is colored blue, as is characteristic of the alkaline salts of 3,3'-dimethoxybenzaurin (VI). But when a stronger alkali is employed, the colored solution begins to be decolorized even while standing, owing to the formation of a salt of the colorless carbinol derivative (VII).



It seemed to us that the formation of a colored solution of the salt of the dye when the bisulfite derivative was reacted directly with an alkali refutes the ester structure (IV), since saponification of such an ester should result in the immediate formation of the colorless salt of the carbinol derivative (VII). But, as has been said, the latter is formed only slowly, as the result of a secondary hydration of the dye salt and only in the presence of a stronger alkali. This is due to the fact that, as our researches have indicated [4], the salts of hydroxyfuchsone dyes and of colorless carbinol derivatives are in equilibrium, the latter being governed by the structure of the dye, the concentration of the alkali, and the temperature. Raising the temperature shifts the equilibrium toward the dye salt, deepening the color; increasing the alkali strength shifts the equilibrium in the opposite direction and weakens the intensity of the color, the solution being wholly decolorized at a certain critical strength.

There was one questionable link in our chain of reasoning, however. It was still not impossible that the substance of the hypothetical structure (IV) decomposed when acted upon by the alkali, giving rise to the dye salt (VI) directly, instead of the salt of the carbinol derivative (VII). We would have to make a study of the saponification of some other substances that were undoubtedly esters of a colorless carbinol derivative of a dye in order to exclude this possibility. A representative of such substances is the acetylation product of 3,3'-dimethoxybenzaurin (III), described in our preceding report [5] and constituting the diacetyl derivative of the corresponding carbinol derivative (VIII). Experiments indicated that the saponification of this ester by a strong alkali

actually did result in the formation of a colorless solution of a salt of the carbinol derivative (VII).



(VIII) (VII)

Similar results were secured when we compared the alkali saponification of acetyl and bisulfite derivatives of other hydroxyfuchsone dyes, such as benzaurin, aurin, and rubrocol. The contrast between the derivatives of 3,3'-dimethoxybenzaurin described above is most striking, however. This contrast is so simple to perform and so significant as to be suitable for lecture demonstration.

For this purpose, 0.01 g of the bisulfite derivative of 3,3'-dimethoxybenzaurin is dissolved in 1 ml of water, while 0.01 g of the acetyl derivative of the dye is simultaneously dissolved in 1 ml of alcohol. The two solutions are then chilled, and 10 ml of a 5% solution of sodium hydroxide is added to each of them. The solution of the bisulfite derivative is instantaneously colored a deep blue. Only after standing for a time is it decolorized, while heating restores a faint color to it. The solution of the acetyl derivative, however, first turns cloudy, owing to the precipitation of the initial substance, which is insoluble in water, but the latter dissolves very quickly, the solution remaining colorless. Only after long standing does the solution become a pale sky-blue; when heated, the color deepens, owing to a shift in the equilibrium, but this color vanishes as the solution cools.

These experiments indicate that the alkaline saponification of the acetyl derivatives of hydroxyfuchsone dyes, which are acetates of the corresponding carbinol derivatives, actually results in the direct formation of colorless salts of the latter. When the bisulfite derivatives of the hydroxyfuchsone dyes are similarly saponified, however, colored salts of the dyes themselves are formed directly, instead of colorless salts of their carbinol derivatives. It follows, therefore, that the bisulfite derivatives of the hydroxyfuchsone dyes are not esters of their carbinol derivatives, which at once eliminated Bayer's hypothesis concerning their structure. The ready formation of the bisulfite derivatives of hydroxyfuchsone dyes, their rapid decomposition by mineral acids and alkalies, and the tendency of the bisulfite derivatives to dissociate when heated that we have observed [3], all support the single conclusion that these substances are formed as the result of the reaction of bisulfite with the carbonyl group of the dye and have the structure of α-hydroxysulfonic acids.

SUMMARY

The alkaline saponification of the acetyl derivatives of hydroxyfuchsone dyes, which are acetates of the corresponding carbinol derivatives, results in

the direct formation of colorless salts of the latter. The similar saponification of the bisulfite derivatives of the hydroxyfuchsone dyes results in the direct formation of colored salts of the dyes themselves. This proves that the bisulfite derivatives of hydroxyfuchsone dyes are not sulfites of the hydroxyfuchsone dyes as Bayer had supposed, but are formed by the reaction of bisulfite with the carbonyl group of the dye and constitute the corresponding α-hydroxysulfonic acids.

LITERATURE CITED

[1] A. Bayer, Ber., 38, 57, (1905).

[2] I. S. Ioffe, J. Gen. Chem. 17, 1916, (1947).

[3] I. S. Ioffe, J. Gen. Chem. 17, 1359, (1947).

[4] I. S. Ioffe, J. Gen. Chem. 19, 911, (1949).*

[5] I. S. Ioffe, J. Gen. Chem. 21, 1316, (1951).**

Received August 19, 1949.

Chair of Organic Chemistry

Academy of Naval Medicine.

*See C.B. Translation, P. 897.

**See C.B. Translation, P. 1439.

RESEARCHES ON THE PHENANTHRENES

I. Synthesis of Phenanthrene Derivatives with Organolithium Compounds

B. M. Mikhailov and N. G. Chernova

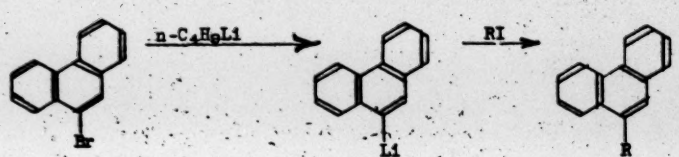
We undertook a study of the chemical transformations of organolithium compounds of phenanthrene to ascertain the feasibility of utilizing this class of organometallic compounds in synthesizing the simplest derivatives of phenanthrene, many of which, as we know, are biologically active. 9-Ethylphenanthrene, for example, manifests the properties of the female sex hormone [1], while phenanthrene-9-carboxylic acid, 9-β-hydroxyethylphenanthrene, and a number of other phenanthrene derivatives can check the growth of malignant tumors [2].

The usual method of synthesizing lithium compounds, involving the action of lithium with halogen derivatives of the hydrocarbons, proved to be inapplicable to the phenanthrenes. According to Müller and Töpel [3], the reaction of 9-bromophenanthrene with lithium is extremely slow, while the 9-phenanthryllithium formed in the reaction is decomposed by the ether employed as a solvent. Gilman and Cook [4] secured lithium compounds of phenanthrene by reacting n-butyllithium with 2-, 3-, and 9-bromophenanthrene. They synthesized phenanthrene-9-carboxylic acid, with a yield of 51%, by boiling an ether solution of the reagents for 4 hours and then carboxylating the reaction products. These findings give us an idea of the stability of a lithium compound of phenanthrene as compared to 9-anthryllithium [5].

We found, however, that such prolonged heating was not necessary for the synthesis of 9-phenanthryllithium, since the reaction of 9-bromophenanthrene with n-butyllithium was very rapid. The finely crystalline organolithium compound of phenanthrene is precipitated as soon as the bromide is added to an ether solution of n-butyllithium, and carboxylating the reaction products 5 minutes later furnished a yield of phenanthrene-9-carboxylic acid that was 85% of the theoretical. When phenyllithium is used instead of n-butyllithium, the 9-phenanthryllithium is not precipitated at once, but after some time has elapsed, crystallizes as large colorless prisms. 9-Phenanthryllithium (I) is extremely reactive, greatly exceeding that of the organomagnesium compound of lithium.

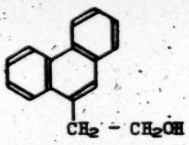
We investigated the action of various reagents, utilized in synthesizing phenanthrene derivatives from 9-phenanthrylmagnesium bromide, upon 9-phenanthryllithium, to secure a comparative evaluation of organolithium and organomagnesium compounds in the synthesis of phenanthrene derivatives. 9-Phenanthrenelithium reacts very energetically with methyl iodide, the reaction being complete within a few minutes. It results in the formation of 9-methylphenanthrene (II, R = CH_3) the yield being 82% of the theoretical.

The organomagnesium compound of phenanthrene, prepared by heating the constituents together for several hours, reacts with methyl iodide to give a 73% yield of 9-methylphenanthrene [6], more than 20 hours of heating being required to complete the reaction. We secured a yield of 52.5% of 9-ethylphenanthrene

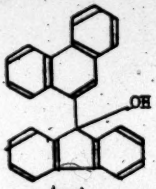


(I) (II) R = CH_3, C_2H_5

(II, R = C_2H_5) by reacting ethyl iodide with 9-phenanthryllithium. This hydrocarbon has been synthesized in the past by reducing 9-acetylphenanthrene [7] (no yield being specified) and in four stages from 2-iodobiphenyl [8]. 9-Phenanthrene reacts instantaneously with chloroformic ester, yielding the ethyl ester of phenanthrene-9-carboxylic acid, which we identified as the free acid. We likewise investigated the behavior of 9-phenanthryllithium with ethylene oxide and fluorenone. The reaction with ethylene oxide was extremely rapid, resulting in the formation of 9-β-hydroxyethylphenanthrene (III), the yield being 59% of the theoretical. When 9-phenanthrylmagnesium bromide was used, the yields of this compound fluctuated from 37 to 50° [9].



(III)

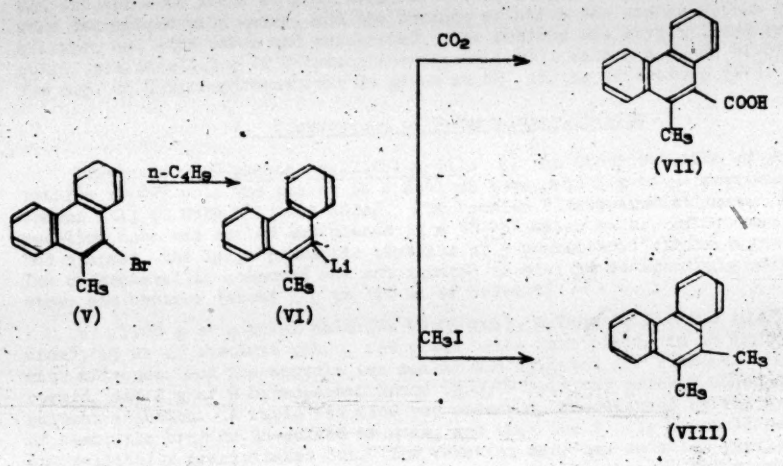


(IV)

The reaction with fluroenone is just as smooth, resulting in biphenylene-9-phenanthrylcarbinol (IV), the yield being 64% of the theoretical. When the organomagnesium compound was used, the yield of the carbinol (IV) was the same [6], but prolonged heating was required to complete the reaction.

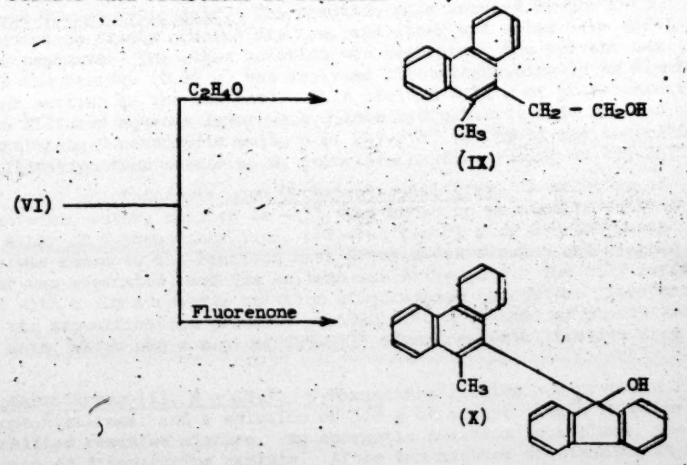
Another compound tested was 9-methylphenanthryl-10-lithium. The initial substance for its preparation was 9-methyl-10-bromophenanthrene (V), which we prepared in two different ways: 1) by reacting 9-methylphenanthrene with bromine directly; and 2) by reacting the hydrocarbon with phosphorus pentabromide. We found that the behavior of the latter reagent with phenanthrene hydrocarbons was exactly like its action upon anthracene and its derivatives [10], i.e., bromine derivatives were formed. The action of phosphorus pentabromide upon phenanthrene results in the formation of 9-bromophenanthrene, though the reaction is not as smooth as in the anthracene series; the bromination of 9-methylphenanthrene with phosphorus pentabromide is quite satisfactory, however, (70% yield) and this method of securing 9-methyl-10-bromophenanthrene. superior to bromination with bromine. When n-butyllithium is reacted with 9-methyl-10-bromophenanthrene in ether, the finely crystalline organolithium

compound of 9-methylphenanthrene (VI) is precipitated at once, its yield being no less than 97%, to judge by the product of its conversion with methyl iodide. Reacting carbon dioxide with 9-methylphenanthryl-10-lithium yields 9-methylphenanthrene-10-carboxylic acid (VII); the reaction with methyl iodide is very smooth, as already stated, yielding 9,10-dimethylphenanthrene (VIII).



(V) (VI) (VII) (VIII)

The reaction of ethylene oxide with 9-methylphenanthryl-10-lithium yields 9-methyl-10-β-hydroxyethylphenanthrene, while biphenylene-9-methylphenanthryl-10-carbinol (X) results when fluorenone is utilized.



EXPERIMENTAL

Action of phorphorus pentabromide upon phenanthrene. 9-bromophenanthrene. 5 g of phenanthrene was dissolved in 15 ml of anhydrous benzene (containing no thiophene), and 14.5 g of finely pulverized phorphorus pentabromide was added to the solution. The reaction flask was closed with a calcium chloride tube and set aside to stand at room temperature for 70 hours. Then the products were decomposed with water, and the benzene solution was washed with a soda solution and with water and evaporated. The residue was crystallized from alcohol, yielding 1.3 g of 9-bromophenanthrene (18%), with a m.p. of 61-63°. The m.p. of 9-bromophenanthrene is given as 63° in the literature [11].

I. Conversions of 9-Phenanthryllithium.

Synthesis of 9-phenanthryllithium (I). a) An ether solution of phenyllithium (0.005 mol) was placed in a Schlenk tube, and 1 g of 9-bromophenanthrene [11] (0.0039 mol) was added. The bromide disappeared at once. The reaction tube was sealed and placed in a 40-45° water bath. After some time had elapsed, the large prismatic crystals of 9-phenanthryllithium began to form. The organometallic compound was not ignited in air; it is sparingly soluble in ether and benzene (about 1 g in 100 ml of solvent).

b) 1.08 g of n-butyl chloride (0.01 mol), 0.22 g of lithium (0.031 gram atom), 15 ml of absolute ether, and glass beads were placed in an ampoule filled with nitrogen, and the ampoule was sealed and agitated for 2 hours. Then it was opened, and 2 g of 9-bromophenanthrene (0.0078 mol) was quickly added to the resultant solution. A rapid reaction was observed, accompanied by the evolution of heat; the bromide dissolved at once, and then the finely crystalline 9-phenanthryllithium precipitated out. The reaction mass was agitated gently for 5 minutes while a gentle current of nitrogen was passed through the ampoule. The organolithium compound of phenanthrene thus secured was utilized in the following experiments.

Phenanthrene-9-carboxylic acid. The reaction mass secured by the method outlined was poured on finely crushed dry ice, and ether and water were added to the reaction products. The ether solution was separated, the solvent was driven off, and the residue (0.29 g) was analyzed chromatographically on alumina (petroleum ether serving as the solvent). This yielded 0.11 g of phenanthrene. Acidulating the filtered aqueous layer with dilute hydrochloric acid yielded 1.46 g of phenanthrene-9-carboxylic acid, m.p. 247-254° (84.6% of the theoretical). After recrystallization from acetic acid, colorless needles fusing at 255-257°.*

Action of ethyl chloroformate upon 9-phenanthryllithium. A solution of 0.5 g of chloroformic ester, chilled to -15°, was added to an equally chilled suspension in ether of 9-phenanthryllium, prepared from 1 g of 9-bromophenanthrene. Water was added to the reaction mass after a few minutes had elapsed, the ether layer was separated, and the solvent was driven off. The oily residue was saponified with a 10% alcoholic solution of potassium hydroxide. Appropriate processing of the saponification products yielded 0.48 g (55.8%) of phenanthrene-9-carboxylic acid, which had a m.p. of 255-257° after recrystallization from acetic acid.

9-Methylphenanthrene (II, R = CH_3). 9-Phenanthryllithium was prepared from 2 g of 9-bromophenanthrene, and a solution of 3.8 g of methyl iodide in ether was added to the chilled reaction mixture. An energetic reaction took place, the organolithium compound disappearing rapidly. After ten minutes of standing at room

* The m.p. given in the literature for phenanthrene-9-carboxylic acid is 251-252°.

temperature, the ether solution was washed with water, and the solvent was driven off. Crystallization of the residue from methanol yielded 1.23 g of 9-methylphenanthrene with a m.p. of 89-90°, or 81.7% of the theoretical yield. Recrystallization from the same solvent yielded the hydrocarbon as colorless, shining platelets, with a m.p. of 90.5-91.5°. The literature gives the m.p. of 9-methylphenanthrene as 90-91.5° [8].

9-Ethylphenanthrene (II, R = CH_3). A solution of 3.8 g of ethyl iodide in ether was added to an organolithium compound of phenanthrene prepared from 2 g of 9-bromophenanthrene. The deposit of 9-phenanthryllithium disappeared after the ampoule was sealed and heated to 50° for 1½ hours of heating. Heating was continued for another 1½ hours, and then the reaction mixture was washed with water, and the solvent was driven off. The oily residue was recrystallized from methanol, yielding 0.81 g of 9-ethylphenanthrene as colorless needles with a m.p. of 60-61.5°. Another 0.03 g of the hydrocarbon (m.p. 60-61.5°) was recovered from the mother liquor via the picrate. The yield totaled 52.5%. The melting points given in the literature for 9-ethylphenanthrene are 61° [7] and 62-63° [8].

9-β-Hydroxyethylphenanthrene (III). A current of ethylene oxide was passed through an ether suspension of 9-phenyllithium for 15 minutes, resulting in the evolution of heat and throwing down an abundant precipitate of lithium alcoholate. The reaction mixture was treated with water, the ether layer was separated, and the solvent was driven off. The residue was crystallized from petroleum ether, yielding 0.51 g of 9-β-hydroxyethylphenanthrene as colorless needles with a m.p. of 87.5-89.5°. The yield was 59.3%. The m.p. of the substance was 90-91° after recrystallization. The literature gives the m.p. of 9-β-hydroxyethylphenanthrene as 92° [8].

Biphenylene-9-phenanthrylcarbinol (IV). A solution of 0.8 g of fluroenone in ether was added to an organolithium compound of phenanthrene prepared from 1 g of 9-bromophenanthrene. The reaction mass was allowed to stand for 30 minutes at room temperature, after which it was washed with water. The residue left after the solvent had been driven off was crystallized twice from benzene and petroleum ether, yielding 0.86 g of biphenylene-9-phenanthrylcarbinol as lustrous prisms with a m.p. of 192.5-194°. Another 0.04 g of the carbinol, with a m.p. of 190-193°, was recovered from the mother liquor. The yield was 64.2%. The substance had a m.p. of 193-194° after another recrystallization from the same solvent. Bachmann [8] gives a m.p. of 189° for biphenylene-9-phenanthrylcarbinol

II Conversions of 9-Methylphenanthryl-10-lithium.

9-Methyl-10-bromophenanthrene (V). a) Bromination of 9-methylphenanthrene with bromine. 1 g of 9-methylphenanthrene and 4 ml of a 1.1 ether-chloroform mixture were placed in a small round-bottomed flask fitted with a thermometer and a dropping funnel, and a solution of 0.83 g of bromine in 1 ml of chloroform was added to the suspension of the hydrocarbon at a temperature that ranged from +8 to -14°. When the reaction was over, the mixture was chilled to -5°, and the yellow precipitate of the bromide was filtered out and washed with cold ether. This yielded 0.41 g of a substance with a m.p. of 117-120°. The mother liquor was evaporated, and the residue was dissolved in benzene and freed of any traces of bromine by washing it with an aqueous solution of soda. The solvent was driven off, and the residue was crystallized from petroleum ether, yielding another 0.44 g of the bromide, with a m.p. of 117-120.5°. The yield totaled 60%. After recrystallization from petroleum ether, the 9-methyl-10-bromophenanthrene consisted of colorless needles with a m.p. of 120.5-122.5°.

2.527 g substance: 6.120 ml CO_2; 1.008 ml H_2O. Found % C 66.09; H 4.46.
$C_{15}H_{11}Br$. Computed % C 66.44; H 4.09.

b) Bromination of 9-methylphenanthrene by phosphorus pentabromide. 8.7 g of finely powdered phosphorus pentabromide was added to a solution of 3.5 g of 9-methylphenanthrene in 35 ml of benzene, placed in a small flask fitted with a calcium chloride tube, and the reaction mixture was allowed to stand at room temperature for 24 hours. All the phosphorus pentabromide dissolved during this time. The benzene solution was washed with water and with a 10% aqueous solution of soda, and the solvent was driven off. Crystallization of the residue from petroleum ether yielded 3.46 g of 9-methyl-10-bromophenanthrene, with a m.p. of 117-120.5° (70.5% yield). The bromide had a m.p. of 120.5-122.5° after recrystallization. A sample of the substance exhibited no depression of the melting point when mixed with 9-methyl-10-bromophenanthrene.

Synthesis of 9-methylphenanthryl-10-lithium. 1 g of 9-methyl-10-bromophenanthrene was added to an ether solution of n-butyllithium, prepared from 0.54 g of n-butyl chloride, 0.1 g of lithium, and 10 ml of ether. The solution turned yellow, and the colorless organolithium compound was precipitated. The mass was agigated gently for 5 minutes, and then the organolithium compound of 9-methylphenanthrene was utilized in the experiments described below.

9-Methylphenanthrene-10-carboxylic acid (VII). A suspension of the organolithium compound was poured over finely crushed dry ice, and then water and ether were added. Acidulation of the aqueous solution yielded 0.6 g of an acid with a m.p. of 196-206° (69.7% of the theoretical). 9-Methylphenanthryl-10-carboxylic acid consisted of colorless needles, with a m.p. of 207.5-208.5°, after crystallization from glacial acetic acid.

2.559 g substance: 7.625 ml CO_2; 1.199 ml H_2O. Found % C 81.31, H 5.24. $C_{16}H_{12}O_2$. Computed % C 81.33, H. 5.11.

9,10-Dimethylphenanthrene (VIII). 1.52 g of methyl iodide dissolved in ether was added to a chilled suspension of the organolithium compound. The mixture heated up, the organometallic compound disappeared, and a colorless cystalline precipitate was thrown down. The mixture was washed with water, the ether was driven off, and the crystalline residue was washed with methanol, yielding 0.74 g of the hydrocarbon as colorless needles with a m.p. of 140-142°. The yield was 97% of the theoretical. The m.p. of the hydrocarbon was 142-142.6° after crystallization from a benzene-alcohol mixture. Zinke [12] gives a m.p. of 139° for 9,10-dimethylphananthrene.

9-Methyl-10-β-hydroxyethylphenanthrene (IX). A current of ethylene oxide was passed through a suspension of the organolithium compound, and the resulting alcoholate was decomposed with water, the ether layer being separated, and the solvent driven off. Crystallization of the residue from petroleum ether yielded 0.57 g of a substance with a m.p. of 117-120° (63.6%). The 9-methyl-10-β-hydroxyethylphenanthrene consisted of colorless crystals with a m.p. of 120-122° after recrystallization from the same solvent.

2.670 mg substance: 8.455 mg CO_2; 1.660 mg H_2O. Found % C 80.42, H 6.96. $C_{17}H_{18}O$. Computed % C 80.50, H. 6.81.

Biphenylene-9-methylphenanthryl-10-carbinol (X). A solution of 0.73 g of fluorenone in ether was added to the organolithium compound. 30 minutes later the reaction mass was treated with water, and the residue left after the ether had been driven off was crystallized from a benzene-petroleum ether mixture. This yielded 0.95 g of a substance in the form of colorless prisms with a m.p. of 204-208°. The yield was 62% of the theoretical. The m.p. of the carbinol was 209.5-210.5° after recrystallization.

2.590 mg substance, 8.560 mg CO_2; 1.307 mg H_2O. Found % C 90.19, H 5.64. $C_{28}H_{20}O$. Computed % C 90.27, H 5.42.

SUMMARY

1. The organolithium compounds of phenanthrene may be utilized in the synthesis of the latter's derivatives. This method of synthesis of phenanthrene derivatives is superior to the method of synthesis involving organomagnesium compounds in point of the speed of the operations involved and in its yields.

2. Several new derivatives of phenanthrene have been synthesized, using organolithium compounds.

3. The reaction of phosphorus pentabromide with phenanthrene and 9-methylphenanthrene results in bromination, yielding 9-bromophenanthrene and 9-methyl-10-bromophenanthrene, respectively.

LITERATURE CITED

[1] Thayer, MacCorquidale and Doiges, J. Pharm. Exp. Therap., 59, 48,(1937).

[2] F. Turner, U.S. Publ. Health Repts., 54,1279, (1939).

[3] E. Müller and T. Töpel, Ber., 72, 273, (1939).

[4] Gilman and T. Cook, J. Am. Chem. Soc., 62, 2813, (1940).

[5] B.M. Mikhailov, Bull. USSR Acad. Sci., Div. Chem. Sci., 4, 420, (1948.

[6] W. Bachmann, J. Am. Chem. Soc., 56, 1363, (1934).

[7] C. Willgerodt and B. Albert, J. prak. chim. (2). 84, 388, (1911).

[8] C. Bradsher and S Amore, J. Am. Chem. Soc., 63, 493, (1941).

[9] E. Bergmann and O. Blum-Bergmann, J. Am. Chem. Soc., 58, 1678,(1936).

[10] B. M. Mikhailov and M. Sh. Promyslov, J. Gen. Chem. 20, 338, (1950).*

[11] E. May and E. Mosettig, J. Org. Chem. (U.S), 11, 15, (1946).

[12] Zinke and Tropp, Ann., 362, 250, (1908).

Received September 15, 1949.

Institute of General and Experimental Pathology, USSR Academy of Medicine.

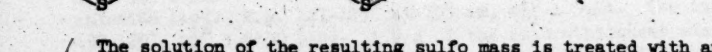
* See C.B. Translation, P. 359.

SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

XVII. The Sulfonation of 2-Chloro-, 2-Bromo-, and 2-Iodothiophenes

A. P. Terentyev and G. M. Kadetsky

As has been reported previously, furan and pyrrole compounds have been successfully sulfonated by the use of pyridine sulfotrioxide [1], an impossibility before the utilization of this method. Thiophene is also distinguished by its marked acidophilic properties [2], though its sulfo acid was prepared by reacting it with sulfuric acid, though the dilution used was very high [3]. Its reaction with pyridine sulfotrioxide involves no tarring at all [1]. It has been found that this method is fully applicable to the halogen derivatives of thiophene, which are much more sensitive than the parent compound, giving high yields of the sulfo derivatives. The methods employed earlier yielded results that were far from satisfactory, owing to the pronounced tarring and the appreciable side reactions. In sulfonating iodothiophene, for example, V. Meyer recommends that batches of a few drops of the substance be used [4]. Investigations of the action of various concentrations of sulfuric acid upon 2-chlorothiophene [5], 2-bromothiophene [6], and 2-iodothiophene [4] showed that the last one, in contrast to the other two, does not yield a pure disulfo acid and is the least stable of the three. W. Steinkopf and his associates employed the brief action of chlorosulfonic acid, with deep chilling, to secure sulfochlorides [7,8]; this increased the yield of the sulfo derivatives, but the yield of pure iodothiophene sulfochloride did not exceed 5%. This method is unsuitable for preparing pure salts of the sulfo acids, though when pyridine sulfotrioxide is employed, they are readily isolated in the pure state. This is done by heating the halogen thiophene with 3 mols of the reagent to 100-120° in a sealed ampoule until the pyridine sulfotrioxide fuses:



The solution of the resulting sulfo mass is treated with an excess of barium carbonate and then evaporated with water until all the pyridine has been eliminated. Filtration yields a solution of the barium salt of the monosulfo acid. Working with barium salts is very convenient, since they can be readily converted into salts of another metal by using a solution of the carbonate or the sulfate. We secured the barium salts of 2-chlorothiophenesulfonic-5 acid (94.8% yield), 2-bromothiophenesulfonic-5 acid (90% yield), and 2-iodothiophenesulfonic-5 acid (77% yield). They were beautiful, lustrous, cubic crystals, that were soluble in water. Reacting their solutions with bromine water yielded a precipitate of barium sulfate – this indicates that the sulfo group is at the α position. When saturated cold solutions of the salts were

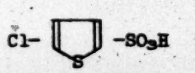
added to α-naphthylmethylthiurone chloride, we secured the low-melting crystalline precipitates of the naphthylmethylthiurone salts of the sulfo acids. These salts were used to prepare the acid chlorides, amides and anilides. The melting points of the derivatives synthesized are like those previously cited by W. F. Steinkopf.

The reaction of halogen thiophenes with pyridine sulfotrioxide is a smooth one. Only in the case of iodothiophene is it complicated by the formation of a slight quantity of 2,5-diiodothiophene. The use of pyridine sulfotrioxide containing 0.5-0.7% of free sulfuric anhydride – "acid" pyridine sulfotrioxide – promotes rearrangement and results in the formation of a mixture of the disulfo acids of iodothiophene and thiophene:

A similar migration of the halogen atom is observed when bromothiophenes [6] and several halogen derivatives of the benzene group are sulfonated with sulfuric acid. With sulfuric acid the instances of migration of the halogen, as well as of the alkyl groups, are so common that they are separated by the so-called Jacobsen reaction [9]. There is no doubt that the influence of chlorosulfonic acid at -15° likewise causes the rearrangement of the iodine in the iodothiophene, since a large amount of the unsubstituted thiophene sulfochloride is formed in addition to the iodothiophene sulfochloride. But this sudden tarring hampers its immediate detection. The utilization of a mild, wholly non-tarring reagent – "acid" pyridine sulfotrioxide – enabled us to discover it. This example demonstrates that the use of pyridine sulfotrioxide may play an important part in the study of dismutations of this type in acidophobic compounds.

EXPERIMENTAL

2-Chlorothiophenesulfonic-5 acid.



The 2-chlorothiophene was prepared by chlorinating thiophene with sulfuryl chloride [10]. B.p. 127-129° at 753 mm, n_D^{20} 1.5476. The literature gives; b.p. 127-129°, n_D^{20} 1.5430 [10]. 1.9 g of the chlorothiophene was sealed in an ampoule with 8 g of pyridine sulfotrioxide. After 8 hours of heating to 120-125°, the contents of the ampoule were a thick liquid of a nearly uniform dark-yellow color, which turned into a light homogeneous crystalline mass when it cooled. It was dissolved in water and treated with 8 g of barium carbonate. The mixture was heated over a water bath until all the pyridine had been driven off. The filtered transparent solution was evaporated until crystallization set in, and the salt was precipitated with an excess of alcohol. The yield was 4.05 g (94.8% of the theoretical). Barium 2-chlorothiophenesulfonate-5 consists of beautiful silver leaflets, soluble in water, more readily so in hot water, and insoluble in alcohol.

13.070 mg substance: 5.310 mg $BaSO_4$. 6.690 mg substance: 2.690 mg $BaSO_4$. Found % Ba 23.91, 23.66. $(C_4H_2O_3S_2Cl)_2Ba$. Computed % Ba 23.99.

It throws down a precipitate of barium sulfate when reacted with bromine water, and a crystalline precipitate of the naphthylmethylthiuronc salt when reacted with a saturated solution of naphthylmethylthiurone chloride.

S-α-naphthylmethyl)-thiuronic salt. A solution of 0.25 g of naphthylmethylthiurone chloride in 5 ml of methanol was added to 0.27 g of the barium salt dissolved in 5 ml of water, and part of the solvent was evaporated at reduced pressure, throwing down the salt almost quantitatively as silky needles collected into sheaves. The m.p. was 138-139° after thorough dessication.

6.020 mg substance: 3.063 ml N_2 (27°, 749 mm). Found % N 6.76
$C_{16}H_{15}O_3ClN_2S_3$. Computed % N 6.75.

2-Bromothiophenesulfonic-5 acid

The 2-bromothiophene was prepared by brominating thiophene with bromine in carbon tetrachloride [11]. B.p. 152-154° at 747 mm. The literature gives the b.p. as 153-154° [11]. 2.9 g of the bromothiophene, 15 g of pyridine sulfotrioxide, and 15 ml of dichloroethane were heated together to 100-105° for 10 hours in a sealed ampoule. 0.3 g of bromothiophene was recovered from the dichloroethane layer. The crystallized layer was dissolved in water and treated as specified above for chlorothiophene. This yielded 7.9 g of glossy lamellar crystals of the barium salt. The yield was about 90% of the bromothiophene placed in the reaction.

6.770 mg substance: 2.475 mg $BaSO_4$. 6.250 mg substance: 2.290 mg $BaSO_4$.
Found % Ba 21.60, 21.56, $C_8H_6O_7Br_2S_4Ba$.

S-(α-naphthylmethyl)-thiuronic salt: Colorless, silky needles, m.p. 142-143°, readily soluble in alcohol and acetone.

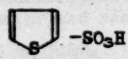
The sulfamide was prepared from the unrefined crystalline sulfochloride. It consisted of colorless crystals with a m.p. of 141-142° after recrystallization from aqueous alcohol. The literature gives the m.p. as 144° [7], p. 148.

4.195 mg substance: 0.2156 ml N_2 (28°, 747 mm). Found % N 5.72.
$C_4H_4O_2BrNS_2$. Computed % N 5.79.

The sulfanilide was prepared by heating the unrefined sulfochloride with an excess of aniline. M.p. 94-95° after recrystallization from aqueous alcohol.

3.700 mg substance: 0.1568 ml N_2 (28°, 749 mm). 3.991 mg substance: 0.1617 ml N_2 (22°, 752 mm). Found % N 4.73, 4.74. $C_{10}H_8O_2BrNS_2$. Computed % N 4.40.

2-Iodothiophenesulfonic-5 acid



The 2-iodothiophene had a b.p. of 79-80° at 20 mm (triple-distilled), which is in conformity with the figure given in the literature [12]. 7.6 g of the iodothiophene was heated to 100-110° for 8 hours in a sealed ampoule with 17.6 g of pyridine sulfotrioxide. As the thick brown liquid cooled it solidified into a dark-yellow mass. The aqueous solution, containing drops of oil, was extracted

with ether, the iodine being eliminated from the ether extract by a solution of sodium sulfite. Evaporation of the ether yielded 0.9 g of the unreacted iodothiophene and 0.13 g of 2,5-diiodothiophene (m.p. of the crude product 35-39°). The aqueous solution was boiled with 18 g of barium carbonate, and then with 5 g of barium hydroxide to eliminate all the pyridine.

The evaporated filtrate yielded minute colorless lamellae of the barium salt, weighing 8.8 g, or approximately 77%, based on the iodothiophene used for the reaction.

3.410 mg substance: 1.135 mg $BaSO_4$. 9.035 mg substance: 3.060 mg $BaSO_4$. Found % Ba 19.50, 19.82. $C_8H_4O_8I_2S_4Ba$. Computed % Ba 19.47.

The potassium salt was prepared by reacting the barium salt with the calculated quantity of potassium carbonate. Colorless, lustrous leaflets, readily soluble in water.

5.275 mg substance: 1.210 mg K_2SO_4. 4.320 mg substance: 0.990 mg K_2SO_4. Found % K 10.27, 10.30. $C_4H_3O_6IS_2K$. Computed % K 10.23.

The S-(α-naphthylmethyl)-thiuronic salt consisted of lustrous acicular crystals. Readily soluble in alcohol and acetone, sparingly in water. M.p. 151-152°.

4.602 mg substance: 0.2401 ml N_2 (30°, 754 mm). Found % N 5.83. $C_{18}H_{16}O_3IN_2S_2$. Computed % N 5.52.

The sulfochloride was a light-yellow acicular mass. M.p. 50-51°. The literature gives the m.p. as 51-52° [7].

The sulfamide consisted of elongated, acicular white crystals (from aqueous alcohol). M.p. 163-164° The literature gives the m.p. was 165° [7].

Found % N 5.18. $C_4H_4O_2INS_2$. Computed % N 5.11.

The sulfanilide consisted of silky acicular crystals, with a m.p. of 124-125° (from aqueous alcohol).

4.490 mg substance: 0.1568 ml N_2 (28°, 756 mm). 5.813 mg substance: 0.2058 ml N_2 (29°, 752 mm). Found % N 3.94, 3.98. $C_{10}H_8O_2INS_2$. Computed % N 3.83.

Reaction of iodothiophene with "acid" pyridine sulfotrioxide. 4.5 g of 2-iodothiophene was heated in a sealed ampoule with 11 g of "acid" pyridine sulfotrioxide to 100° for 12 hours and to 130° for 2 hours until a homogeneous mass had been formed. The brown crystalline mass was then dissolved in water. The insoluble flakes, totaling 1.05 g, were filtered out. Yellowish minute lamellae after recrystallization from petroleum ether (the solution being treated with sodium sulfite to bind the free iodine). M.p. 41.8 42°. The literature gives the m.p. of 2,5-diiodothiophene as 40.5-41.5° [13]. Processing of the aqueous solution yielded 6.5 g of a crystalline powder, recrystallization of which yielded barium iodothiophenesulfonate - lamellar crystals that are slightly soluble in cold water and readily soluble in hot.

4.000 mg substance: 1.870 mg $BaSO_4$. 6.735 mg substance: 3.125 mg $BaSO_4$. Found % Ba 27.52 27.31. $C_4HO_6IS_2Ba$. Computed % Ba 27.01

The residue consists of a mixture of equimolecular quantities of the barium salts and the disulfo acids of thiophene and iodothiophene that was hard to separate.

SUMMARY

Pyridine sulfotrioxide has been utilized to sulfonate 2-chlorothiophene, 2-bromothiophene, and 2-iodothiophene without a trace of tarring. The barium salts of the following acids have been synthesized: 2-chlorothiophenesulfonic-5 acid (94.8% yield); 2-thiophenesulfonic-5 acid (90% yield); and 2-iodothiophenesulfonic-5 acid (77% yield), together with other salts and derivatives of these sulfo acids.

It has been shown that the reaction of iodothiophene with normal and "acid" pyridine sulfotrioxide involves dismutation of the halogen.

LITERATURE CITED

[1] A. P. Terentyev, Bull. Moscow State University 1947, 6, 9-32; A. P. Terentyev and L. A. Kazitsina, Proc. USSR Acad. Sci., 51, 603, (1945); A. P. Terentyev and L. A. Yanovskaya, Report XVI, J. Gen. Chem. 21, 1295,(1951).

[2] A. Töhl, Ber., 27, 665, (1894); Houben, Methods of Organic Chemistry, (Russ. Ed.) Vol. III, Part 3, 553, (1935).

[3] V. Meyer, Die Thiophengruppe, p. 111-117, Braunschweig, 1888; V. Meyer, Ber., 16, 1471, (1883); Lieb. Ann., 236, 206, (1886).

[4] V. Meyer, Die Thiophengruppe, 138-139; J. Langer, Ber., 18, 553,(1885).

[5] A. Töhl, O. Eberhard, Ber., 26, 2947, (1893).

[6] A. Töhl, K. Schultz, Ber., 27, 2834, (1894).

[7] W. Steinkopf, H. Jacob, H. Penz, Lieb. Ann., 512, 136, (1934).

[8] W. Steinkopf, W. Köhler, Lieb. Ann., 532, 250, (1937).

[9] Organic Reactions,(Russ. Ed.), Vol. I., p. 492. Moscow, (1948).

[10] E. Campaigne, W.M. Suer, J. Am. Chem. Soc., 70, 415, (1948).

[11] F. F. Blicke, J. H. Burkhalter, J. Am. Chem. Soc., 64, 477,(1942).

[12] Syntheses of organic preparations, Vol. 3., p. 49. Moscow (1935).

[13] W. Steinkopf, M. Bauermeister, Lieb. Ann., 403, 62 (1914).

Received October 7, 1949.

The N.D. Zelinsky Laboratory
of Organic Chemistry
Moscow State University

THE N-ARYL AMIDES OF HYDROXY ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS *

II. Naphthalides of α-Hydroxy Carboxylic Acids

P. A. Petyunin and N. G. Panferova

In our first report we showed that the principal reaction products may be anilides of the α-keto or α-hydroxy acids, depending on the ratio between the organomagnesium compound and the oxanilic ester.

To check this hypothesis, and to extend the field of utilization of this reaction, we undertook further investigations with a view to determining the part played by the radical attached to the nitrogen in setting up steric hindrances, making a study of the reaction between organomagnesium compounds and the esters of α- and β-naphthyloxaminic acid. According to the literature [2], α-naphthyl is an orthosubstituted radical and hence ought to be extremely active sterically.

The reaction was carried out with various numbers of mols of the Grignard reagent, depending upon the objective of the test.

In contrast to the oxanilic ester, the formation of keto acid derivatives is much easier with the α- and β-naphthyloxaminic esters. Whereas certain precautions have to be employed with the former, such as deep chilling when the reagents are mixed together and when the reaction mass is decomposed, these precautions are not obligatory with the naphthyloxaminic esters.

Replacing the phenyl radical by naphthyl increases the steric hindrances. As we know, the reaction of esters with a Grignard reagent takes place via a stage in which ketones are formed [3]. The ketones may be isolated, however, whenever structural factors result in the appearance of steric hindrances, either because of the organomagnesium compound [4] or the ester [5]. In the reaction we have been investigating, the steric hindrances appeared in the N-aryl oxaminic ester. When a large quantity of a Grignard reagent (4-5 mols) is reacted with naphthyloxaminic esters, the principal reaction products will be the naphthalides of α-hydroxy acids. As in the oxanilic ester, the excess Grignard reagent acts as a solvent, increasing the yield of the hydroxy acid naphthalides. We have investigated the reaction of ethyl esters of α- and β-naphthyloxaminic acid with RMgX, where R = CH_3, C_2H_5, iso-C_5H_{11}, C_6H_5, and n − $CH_3C_6H_4$.

The properties of the synthesized compounds are listed in the subjoined table.

The α- and β-naphthalides of α-isobutyric acid are described in the literature, the other compounds having been synthesized by us for the first time. The reaction of the ethyl esters of α- and β-naphthyloxaminic acids and organomagnesium compounds may be recommended as a preparative method for securing the naphthalides of α-keto and α-hydroxy acids.

---

* The first report was published under the following title: "The Action of a Grignard reagent upon esters of N-substituted amides of dicarboxylic acids".

No.	Naphthalide formula	Melting Point, °	M.p. given in literature, °
1	α-$C_{10}H_7NHCO\cdot C(OH)(CH_3)_2$	159.5°	159.5 – 161°[6]
2	α-$C_{10}H_7NHCO\cdot C(OH)(C_2H_5)_2$	140.5	
3	α-$C_{10}H_7NHCO\cdot C(OH)(iso\text{-}C_5H_{11})_2$	140.5	
4	α-$C_{10}H_7NHCO\cdot C(OH)(C_6H_5)_2$	195	
5	α-$C_{10}H_7NHCO\cdot C(OH)(n\text{-}C_6H_4CH_3)_2$	151	
6	α-$C_{10}H_7NHCO\cdot COC_2H_5$	173	
7	β-$C_{10}H_7NHCO\cdot C(OH)(CH_3)_2$	157	157 – 159° [7]
8	β-$C_{10}H_7NHCO\cdot C(OH)(C_2H_5)_2$	124.5	
9	β-$C_{10}H_7NHCO\cdot C(OH)(iso\text{-}C_5H_{11})_2$	129	
10	β-$C_{10}H_7NHCO\cdot C(OH)(C_6H_5)_2$	201	
11	β-$C_{10}H_7NHCO\cdot C(OH)(n\text{-}C_6H_4CH_3)_2$	191	
12	β-$C_{10}H_7NHCO\cdot COC_2H_5$	170.5	

EXPERIMENTAL

α-Naphthalide of α-hydroxyisobutyric acid. The α-naphthalide of α-hydroxyisobutyric acid was synthesized by reactin 4.4 mol of methylmagnesium iodide, prepared from 20.5 g of methyl iodide and 3.5 g of magnesium in 70 ml of ether, with 8 g (1 mol) of α-naphthyloxaminic ester.* This yielded 6 g of the substance, or 80% of the theoretical yield. It was a finely crystalline powder, with a m.p. of 159.5° after crystallization from alcohol. The literature gives the m.p. of the α-naphthalide of α-hydroxyisobutyric acid as 159-161° [6].

0.3431 g substance: 15 ml 0.1 N H_2SO_4 (Kjeldahl). 0.2261 g substance: 10.1 ml 0.1 N H_2SO_4. Found % N 6.12, 6.26. $C_{14}H_{15}O_2N$. Computed % N 6.15.

α-Naphthalide of diethylglycolic acid. The following quantities were used in this reaction: 8 g (1 mol) of the ethyl ester of α-naphthyloxaminic acid, 22.6 g of ethyl iodide (4.4 mols), and 3.5 g of magnesium. The yield was 6.6 g of the substance, or 78.5% of the theoretical. The naphthalide is insoluble in water, slightly soluble in benzene and ether, and readily soluble in alcohol and acetone. It crystallizes from alcohol as colorless lamellae with a m.p. of 140.5°.

0.2026 g substance: 7.89 ml 0.1 N H_2SO_4. Found % N 5.45. $C_{16}H_{19}O_2N$. Computed % N 5.44.

α-Naphthalide of diisoamylglycolic acid. The α-naphthalide of diisoamylglycolic acid was prepared from 6.6 g (1 mol) of the ethyl ester of α-naphthyloxaminic acid, 17.9 g of isoamyl bromide (4.4 mols) and 2.8 g of magnesium. The yield was 5.6 g, or 60.8% of the theoretical. Elongated thin needles with a m.p. of 140.5° after crystallization from dilute alcohol. The naphthalide is insoluble in water, but freely soluble in alcohol, ether, benzene and acetone.

0.2558 g substance: 6.76 ml 0.1 N H_2SO_4. 0.3011 g substance: 8.4 ml 0.1 N H_2SO_4. Found % N 3.7, 3.91. $C_{22}H_{31}O_2N$. Computed % N 4.1.

α-Naphthalide of diphenylglycolic acid. (α-naphthalide of benzylic acid). The initial substances were: 8 g (1 mol) of the ethyl ester of α-naphthyloxaminic acid, 22.7 g (4 mols) of bromobenzene, and 3.5 g of magnesium. The yield was 11 g, or 94.8% of the theoretical. The naphthalide is insoluble in water or

*The α-naphthyloxaminic ester was prepared by heating α-naphthylamine with ethyl oxalate.

ether, slightly soluble in cold alcohol and benzene, and readily soluble when heated in the latter two solvents. It turns concentrated sulfuric acid a disappearing red. It was crystallized from alcohol as elongated thin needles with a m.p. of 193°. Recrystallization from benzene raised the m.p. to 195°.

0.2152 g substance: 6.44 0.1 N H_2SO_4. Found % N 4.19. $C_{24}H_{19}O_2N$. Computed % N 3.96.

α-Naphthalide of n,n'-ditolylglycolic acid. (α-naphthalide of p-toluic acid). The initial substances used were: 5 g of the ethyl ester of α-naphthyloxaminic acid in 30 ml of ether, 15.5 g of p-bromotoluene, and 2.2 g of magnesium. The yield was 7.1 g, or 91% of the theoretical. The naphthalide is insoluble in water or petroleum ether, though freely soluble in alcohol, ether, dichloroethane, and benzene. It dissolves in concentrated sulfuric acid, turning it a dark crimson, which disappears. A finely crystalline powder with a m.p. of 151° after crystallization from a small quantity of alcohol.

0.2056 g substance: 5.58 ml 0.1 N H_2SO_4. Found % N 3.79. $C_{26}H_{23}O_2N$. Computed % N 3.67.

α-Naphthalide of propionylformic acid. The initial substances used were: 5 g (1 mol) of the α-naphthyloxaminic ester, 7.1 g (2.2 mols) of ethyl iodide, and 1.1 g of magnesium. Toward the end, the reaction mass was heated for 30 minutes over a water bath. No heat was evolved when a saturated solution of ammonium chloride was added. The precipitated substance was insoluble in water or the usual organic solvents. It decomposed without melting when placed in the flame of an alcohol lamp. It contained halogen (Beilstein test) and magnesium (reaction with an alkaline solution of p-nitrobenzeneazoresorcinol [9]). The reaction product was washed with water and triturated in a mortar with 15 ml of dilute sulfuric acid, which caused the reaction mass to give off heat and to foam. The precipitate was then washed with water until its reaction was neutral and dried in the air. The naphthalide is insoluble in water, but freely soluble in most of the customary organic solvents. It crystallizes from toluene as elongated needles with a m.p. of 173°.

0.2068 g substance: 9.13 ml 0.1 Na H_2SO_4. Found % N 6.18. $C_{14}H_{13}O_2N$. Computed % N 6.17.

β-Naphthalide of α-hydroxybutyric acid. The β-naphthalide of α-hydroxybutyric acid was synthesized from 10 g (1 mol) of the ethyl ester of β-naphthyloxaminic acid, 25.6 g (4.4 mols) of methyl iodide, and 4.4 g of magnesium.

It crystallized from alcohol as small lamellae with a m.p. of 157°. The yield was 8 g, or 84.9% of the theoretical.

0.1717 g substance; 7.5 ml 0.1 N H_2SO. 0.1131 g substance: 5.1 ml 0.1 N H_2SO_4. Found % N 6.11, 6.31. $C_{14}H_{15}O_2N$. Computed % N 6.15.

The naphthalide of α-hydroxyisobutyric acid was synthesized by reacting an alcoholic solution of potassium hydroxide with the β-naphthalide of α-bromoisobutyric acid as well as by heating α-hydroxyisobutyric acid with β-naphthylamine. M.p. 157-159° [7].

β-Naphthalide of diethylglycolic acid. The initial substances used were: 10 g of the ethyl ester of β-naphthyloxaminic acid, 28.2 g of ethyl iodide, and 4.4 g of magnesium. This yielded 9.5 g, or 90.4% of the theoretical. The naphthalide is insoluble in water, slightly soluble in carbon tetrachloride, gasoline, and toluene, and readily soluble in ether, acetone, and alcohol. It crystallized

---

* The β-naphthyloxaminic ester was prepared from β-naphthylamine and ethyl oxalate. M.P. 119-120° [10].

from alcohol as minute needles with a m.p. of 124.5°.

0.2836 g substance: 10.38 ml 0.1 N. H_2SO_4. 0.1411 g substance: 5.2 ml 0.1 N. H_2SO_4. Found % N 5.42, 5.16. $C_{16}H_{19}O_2N$. Computed % N 5.44.

β-Naphthalide of propionylformic acid. The initial substances used were: 5 g (1 mol) of the ethyl ester of β-naphthyloxaminic acid, 7.1 g (2.2 mols) of ethyl iodide, and 1.1 g of magnesium. The reaction mass was treated with a saturated solution of ammonium chloride, and the precipitate was heated to boiling with a small quantity of alcohol. Driving off the alcohol yielded a small quantity of a substance with a m.p. of 121° – the impure β-naphthalide of diethylglycolic acid (m.p. of the pure substance 124.5°). The principal reaction product contained halogen and magnesium and was isolated like the α-naphthalide of propionylformic acid. The naphthalide is insoluble in water, slightly soluble in ether and chloroform, and readily soluble in alcohol, acetone, and carbon tetrachloride. Elongated needles in clusters, with a m.p. of 170.5°, when crystallized from carbon tetrachloride. The yield was 3.5 g, or 79.6% of the theoretical.

0.1548 g substance: 6.76 ml 0.1 N H_2SO_4. 0.1233 g substance: 5.2 ml 0.1 N H_2SO_4. Found % N 6.11, 5.9. $C_{14}H_{13}O_2N$. Computed % N 6.17.

β-naphthalide of diisoamylglycolic acid. The initial substances used were: 8 g (1 mol) of the ethyl ester of β-naphthyloxaminic ester, 21.8 g (4.4 mols) of isoamyl bromide, and 3.5 g of magnesium. The yield was 9.3 g or 83% of the theoretical. The naphthalide is insoluble in water, slightly soluble in benzene and carbon tetrachloride, and freely soluble in alcohol, ether, and chloroform. Elongated colorless needles with a m.p. of 129° when crystallized from alcohol.

0.2460 g substance: 7.51 ml 0.1 N H_2SO_4. 0.1476 g substance: 4.2 ml 0.1 N H_2SO_4. Found % N 4.27, 3.98. $C_{22}H_{31}O_2N$. Computed % N 4.1.

β-Naphthalide of diphenylglycolic acid. (β-naphthalide of benzylic acid). The following substances were used in synthesizing the β-naphthalide of benzylic acid: 8 g (1 mol) of the ethyl ester of β-naphthyloxaminic acid, 22.7 g (4.4 mols) of bromobenzene, and 3.5 g of magnesium. The yield was 9 g, or 77.6% of the theoretical. Colorless needles, with a m.p. of 201°, when crystallized from alcohol. The naphthalide is insoluble in water; slightly soluble in ether and carbon tetrachloride, and freely soluble in chloroform, acetone and benzene. It dissolves in concentrated sulfuric acid, turning the solution red, the color quickly changing to greenish and then disappearing altogether.

0.2420 g substance: 7.2 ml 0.1 N H_2SO_4. 0.1602 g substance: 4.4 ml 0.1 N H_2SO_4. Found % N 4.16, 4.29. $C_{24}H_{19}O_2N$. Computed % N 3.96.

β-Naphthalide of p-ditolylglycolic acid. (β-naphthalide of p-toluic acid). The initial substances used were: 5 g (1 mol) of the ethyl ester of β-naphthyloxaminic acid, 15.5 g (4.4 mols) of p-bromotoluene, and 2.2 g of magnesium. This yielded 7.1 g of the substance, or 91% of the theoretical. It was purified by crystallization from alcohol. Minute needles with a m.p. of 191°. The naphthalide is insoluble in water, slightly soluble in benzene and toluene, and freely soluble in other customary organic solvents. It dissolved in concentrated sulfuric acid, turning the solution dark crimson, the color disappearing upon standing.

0.2478 g substance: 7 ml 0.1 N H_2SO_4. Found % N 3.95. $C_{28}H_{23}O_2N$. Computed % N 3.67.

SUMMARY

1. A study has been made of the reactions of organomagnesium compounds with the ether esters of α- and β-naphthyloxaminic acids. It has been shown that the principal reaction products are naphthalides of α-keto or α-hydroxy acids, depending upon the proportions of the reagents used.

2. The ease with which the naphthalides of the α-keto acids are formed is due to the manifestation of a steric effect at the aryl amide radical.

3. Several α- and β-naphthalides of α-keto and α-hydroxy acids hitherto unknown in the literature have been synthesized and their properties described.

4. The reaction of organomagnesium compounds with the ethyl esters of α- and β-naphthyloxaminic acids may be recommended for the synthesis of naphthalides of α-keto and α-hydroxy acids.

LITERATURE CITED

[1] J. Gen. Chem. 17, 502, (1947).

[2] I. I. Lapkin and assoc., J. Gen. Chem. 17, 1333, (1947).

[3] F. Runge, Organomagnesium compounds (Russ. Ed.), p. 123, United Sci. and Tech. Press, (1937).

[4] E. Bergmann and H. Weib, Ber, 64, 485, (1931); A. Spasov, Zbl., 1905, I, 1572: I. I. Lapkin, J. Gen. Chem. 16, 724, (1946).

[5] A. Guyot and Catel, Zbl., 1905, I, 679.

[6] K. Bischoff and P. Walden, Lieb. Ann., 279, 117, (1894).

[7] K Bischoff and P. Walden, J. Russ. Chem. Soc. 26, 184, (1894); Tigerstadt, Ber., 25, 2930, (1892); 279, 112, 1894.

[8] Ballo, Ber., 6, 247, (1873).

[9] L. M. Kulberg, J. Gen. Chem. 8, 1132, (1938); Syntheses of organic preparations, p. 97, State Chemical Press, (1947).

[10] R. Maeyer and Müller, Ber., 30, 772, (1897).

Received September 22, 1949.

Laboratory of Organic Chemistry
Molotov Pharmaceutical Institute.

THE N-ARYL AMIDES OF HYDROXY ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

III. The Reactions of Organomagnesium Compounds with the Esters of Ortho-Methoxymalonanilic and Succinanilic Acids

Synthesis of the Anilides of γ-Hydroxy Acids

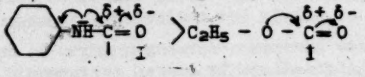
P. A. Petyunin and N. G. Panferova

According to Slavyanov [1], Valeur [2], Dielthey and Last [3], Witting and Leo [4], and other research workers, malonic ester and its alkyl-substituted derivatives react with organomagnesium compounds to form tertiary glycols, ketols, and the like, the second ester group being much more difficult to involve in the reaction than the first one. According to the literature, the reaction between orthomethoxymalonanilic ester and organomagnesium compounds ought to entail the formation of aryl amides of β-hydroxy acids as follows:

$$R - NH - CO - CH_2 - COOR' \xrightarrow{2R''MgX} R - NH - CO - CH_2 - C(OH)R_2''.$$

Large quantities of gas were evolved when methylmagnesium iodide or ethylmagnesium iodide was added.* After the reaction mass was decomposed, we secured the orthomethoxymalonanilic ester unchanged, it being identified by the melting point of a sample mixed with a sample of the known substance. In no case did we find the aryl amide of a β-hydroxy acid. This phenomenon is evidently attributable to the fact that orthomethoxymalonanilic ester reacts in the enol form. This is evidenced by the results of our experiments and by the evolution of 2 mols of methane in the reaction with methylmagnesium iodide. Ivanov and Spasov [5] found that isopropylmagnesium chloride reacts with malonic ester, yielding a large amount of gas, consisting mainly of propane. The authors explain this by the fact that the malonic ester reacts in the enol form. Job and Reich [6] found that malonic ester reacts with ethylzinc iodide in the enol form. The reaction of orthomethoxymalonanilic ester in its enol form may be attributable to its greater enolization than is the case with malonic ester, inasmuch as the aryl amid group is a much stronger group than the carbethoxy one insofar as its enolizing influence is concerned [7].

The unshared electron pair in the nitrogen atom of the aryl amid group will be repelled by the benzene ring, besides being shifted toward the carbonyl group. This entails a decrease in the extent of the neutralization of the tial positive charge on the C=O carbon atom, while the aryl amide group will act as a stronger activator of prototropic systems than the carbethoxy group:



---

* The Chugaev-Tserevitinov method was used to determine that two moles of methane are evolved in the reaction with methylmagnesium iodide.

The experiments utilizing succinanilic ester were made with various numbers of mols of the organomagnesium compound.

When the succinanilic ester was reacted with 1 mol of an organomagnesium compound, only part of it entered into the reaction, forming an aryl amide of a γ-hydroxy carboxylic acid, the bulk of it being recovered unchanged (Experiment 1, Table 1). No aryl amide of a γ-keto acid was discovered among the reaction products. Under these conditions, as well as when 2 mols of the reagent are used, the derivatives of the oxaminic ester readily form aryl amines of the α-keto acids [8]. The hindrances noted above in the oxaminic ester with respect to organomagnesium compounds are not manifested in the latter's reactions with succinanilic ester. As the amount of Grignard reagent used increases, the yield of the aryl amid of the hydroxy acid rises.

TABLE

No.	Grams of ester	Mols of organo-magnesium compound	Yield of Reaction Product: Ether-insoluble portion (initial product)		Ether soluble portion (anilide of a hydroxy acid)	
			grams	%	grams	%
1	2	1	1	50	0.5	22
2	2	2	0.5	25	1	44
3	2	3	negligible	–	1.2	52.8
4	2	4	traces	–	1.3	57.8

The maximum yields are secured when 3-4 mols of the organomagnesium compound are reacted with 1 mol of the ester (Experiments 3 and 4). The general equation for the formation of aryl amides of the hydroxy acids may be stated as follows:

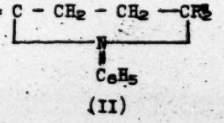
$$RNH - CO - CH_2 - CH_2 - COOR' \xrightarrow{2R''MgX} R - NH - CO - CH_2 - CH_2 - C(OH)R''_2$$

The presence of mobile hydrogen at the nitrogen atom and of a hydroxyl group at the γ- carbon atom makes it not altogether impossible that water is evolved intramolecularly and a lactam is formed. Abkin and Medvedyev [9] have described the formation of a lactam of santoninic acid from its amide.

The N-phenyllactum (II) may be formed alongside the anilide of the γ-hydroxy acid (I):

$$C_6H_5NH - CO - CH_2 - CH_2 - C(OH)R''_2$$

(I)



(II)

From a determination of their active hydrogen, we deduced the structure of the synthesized compounds to be that of anilides of -hydroxy acids. The properties of the compounds synthesized are listed in Table 2:

The reaction of organomagnesium compounds with succinanilic ester may be recommended as a preparative method of synthesizing the N-aryl amides of γ- hydroxy acids.

TABLE 2

No.	Anilide formula	M.p.,	Active hydrogen	
			Found	Calculated
1	$C_6H_5NH-CO-CH_2-CH_2-C(OH)(CH_3)_2$.....	91.5°	1.97	2
2	$C_6H_5NH-CO-CH_2-CH_2-C(OH)(C_2H_5)_2$.....	82.5	1.88	2
3	$C_6H_5NH-CO-CH_2-CH_2-C(OH)(C_5H_{11}\text{-iso})_2$	81.5	-	-
4	$C_6H_5NH\ CO\ CH_2\ CH_2\ C(OH)(C_3H_5)_2$.....	89.5-90.5	-	-
5	$C_6H_5NH\ CO\ CH_2\ CH_2\ C(OH)(C_8H_4OCH_3)_2$.	168-170	-	-

EXPERIMENTAL

Ethyl ester of orthomethoxymalonanilic acid 5 g (1 mole) of orthoanisidine was heated with 7.1 g (1.1 mole) of malonic ester over a sand bath for 3-4 hours, heating being continued until a sample crystallized completely. The reaction mass was poured into 50 ml of hot alcohol, the resultant precipitate being filtered out and recrystallized from alcohol. Colorless needles with a m.p. of 159.5°. The yield was 1.6 g of the diorthoaniside of malonic acid.

0.5558 g substance: 69.25 ml 0.05 N H_2SO_4 (Kjeldahl). Found %: N 8.72.
$C_{17}H_{18}O_4N_2$. Computed %: N 8.91.

The diorthoaniside of malonic acid is not described in the literature. The main reaction product was precipitated by diluting the filtrate with water, the precipitated heavy, oily liquid being treated with dilute hydrochloric acid (to eliminate the unreacted anisidine) and then washed with water. Rubbing with a glass rod caused a crystalline mass to form. The yield was 3.7 g, or 38.5% of the theoretical. Crystallized from benzene as colorless lamellae with a m.p. of 63°. The substance is insoluble in water, slightly soluble in ether and cold benzene, and freely soluble in other organic solvents.

0.4216 g substance: 36.7 ml 0.05 N H_2SO_4. Found %: N 6.09.
$C_{12}H_{15}O_4N$. Computed %: N 5.9.

Orthomethoxymalononanilic acid. 1 g of the ethyl ester of orthomethoxymalonanilic acid was heated over a water bath with 10 ml of a 10% solution of sodium hydroxide until it all dissolved. After the solution had cooled, concentrated hydrochloric acid was added to the solution until its reaction was acid with congo red, and the resultant precipitate was isolated in the usual manner. Crystallized from water as colorless prisms with a m.p. of 145° (with decomposition, CO_2 being evolved). Orthomethoxymalonanilic acid is not described in the literature. It decomposed when heated, yielding acetanisidine, with a m.p. of 86° [10], as shown below.

The anilide of γ,γ-dimethyl-γ-hydroxybutyric acid. The initial substances used were: 5 g (1 mole) of the methyl ester of succinanilic acid,* 10.3 g (3 moles) of methyl iodide, and 1.8 g of magnesium. This yielded 2.2 g, or 44% of the theoretical. The anilide is insoluble in water, slightly soluble in petroleum

* The methyl ester of succinanilic acid was secured by heating succinanil, m.p. 152° [11], with methanol and concentrated sulfuric acid. M.P. of the ester 97-98°, which is the figure given in the literature [12].

ether, benzene, and toluene, and readily soluble in alcohol, acetone, and chloroform. It crystallized from gasoline as minute colorless needles with a m.p. of 91.5°.

0.2104 g substance: 10.11 ml 0.1 N H_2SO_4; 0.2161 g substance: 6 ml 0.1 N H_2SO_4. 0.1136 g substance: 26 ml CH_4 (18°, 753.5 mm) (Chugaev-Tserevitinov). Found %: N 6.72, 6.66. H· 1.97. $C_{12}H_{17}O_2N$. Computed %: N 6.76; H· 2.

The anilide of γ,γ-dimethyl-γ-hydroxybutyric acid is not described in the literature.

Anilide of γ,γ-diethyl-γ-hydroxybutyric acid. The initial substances used were: 2 g (1 mole) of the ethyl ester of succinanilic acid, 4.5 g (3 moles) of ethyl iodide, and 0.7 g of magnesium.

This yielded 1.2 g, or 52.8% of the theoretical. The anilide is slightly soluble in water, petroleum ether, gasoline, and carbon tetrachloride, and freely soluble in the other customary organic solvents. It crystallized from petroleum ether as elongated colorless needles with a m.p. of 82.5°.

0.2108 g substance: 8.71 ml 0.1 N H_2SO_4. 0.2058 g substance: 8.49 ml 0.1 N H_2SO_4. 0.0858 g substance: 16.5 ml CH_4 (19°, 756 mm). Found %: N 5.78, 5.77; H· 1.88. $C_{14}H_{21}O_2N$. Computed %: N 5.95; H· 2.

The anilide of γ,γ-diethyl-γ-hydroxybutyric acid is not described in the literature.

Anilide of γ,γ-diallyl-γ-hydroxybutyric acid. The initial substances used were: 5 g (1 mole) of succinanilic ester, 8.7 g (3 moles) of allyl bromide, and 1.8 g of magnesium. The anilide is insoluble in water, slightly soluble in toluene and carbon tetrachloride, and readily soluble in alcohol. It crystallized from carbon tetrachloride as needles with a m.p. of 89.5-90.5°. The yield was 3.4 g, or 54.8% of the theoretical.

0.2216 g substance: 9.03 ml 0.1 N H_2SO_4. 0.2266 g substance: 9.25 ml 0.1 N H_2SO_4. Found %: N 5.7, 5.71. $C_{16}H_{21}O_2N$. Computed %: N 5.4.

The anilide of γ,γ-diallyl-γ-hydroxybutyric acid is not described in the literature.

Anilide of γ,γ-diisoamyl-γ-hydroxybutyric acid. The following were used synthesize the anilide of γ,γ-diisoamyl-γ-hydroxybutyric acid: 5 g (1 mole) of the methyl ester of succinanilic acid, 10.4 g (3 moles) of isoamyl bromide, and 1.8 g of magnesium. The yield was 2.8 g, or 36.3% of the theoretical.

The anilide is insoluble in water, slightly soluble in carbon tetrachloride, gasoline, and petroleum ether, and readily soluble in benzene, toluene, acetone and alcohol.

0.1590 g substance: 9.9 ml 0.05 N H_2SO_4; 0.1273 g substance: 8.13 ml 0.05 N H_2SO_4. Found %: N 4.36, 4.47. $C_{20}H_{33}O_2N$. Computed %: N 4.39.

The anilide of γ,γ-diisoamyl-γ-hydroxybutyric acid is not described in the literature.

The anilide of γ,γ-bis-(2-methoxyphenyl)-γ-hydroxybutyric acid. The initial substances used were: 5 g (1 mole) of succinanilic ester, 16.9 g (3 moles) of orthoiodoanisole, and 1.7 g of magnesium. The reaction mass was decomposed with with a saturated solution of ammonium chloride, and the reaction product was extracted with ether. Evaporating the solvent yielded an oily liquid that slowly crystallized. The yield was 6.9 g, or 73.4% of the theoretical. The anilide is insoluble in water, slightly soluble in gasoline and carbon tetrachloride, and freely soluble in benzene, toluene, and alcohol. It dissolved in concentrated

sulfuric acid, turning the solution red-violet, the color slowly changing into brown, and crystallized from toluene as colorless needles with a m.p. of 168-170°.

0.4032 g substance: 10.3 ml 0.1 N H_2SO_4: 0.3100 g substance: 8.2 ml 0.1 N H_2SO_4. Found %: N 3.58, 3.7. $C_{24}H_{25}O_4N$. Computed %: N 3.57.

The anilide of γ,γ-bis-(2-methoxyphenyl)-γ-hydroxybutyric acid is not described in the literature.

SUMMARY

1. Orthomethoxymalonanilic ester evidently reacts withorganomagnesium compounds in its enol form, being recovered unchanged after the reaction mass is decomposed.

2. A study has been made of the reaction of succinanilic ester with organomagnesium compounds, it being found that only the carbethoxy group of the succinanilic ester enters into the reaction, giving rise to anilides of the γ-hydroxy carboxylic acids. This reaction is suitable as a preparative method of synthesizing the aryl amides of γ-hydroxy acids.

3. The steric hindrances observed by us in the case of derivatives of oxaminic ester are not manifested in the reaction of succinanilic ester with organomagnesium compounds.

4. Several anilides of the γ-hydroxy acids hitherto unknown in the literature have been synthesized and their properties investigated.

LITERATURE CITED

[1] Slavyanov, J.Russ.Chem.Soc. 39, 140 (1907).

[2] Valeur, Chem. Zentr., 1901, I, 999.

[3] Dielthey and Last, Ber., 37, 2639 (1904); Chem. Zentr. 1916, II, 1028.

[4] Wittig and Leo, Ber., 62, 1409 (1929).

[5] D. Ivanov and A.Spasov, Bull. Soc. Chim. France (5), 1, 1419 (1934).

[6] Bull. Soc. Chim. France, 33, 1414 (1923).

[7] F.O.Rice. Mechanism of Homogeneous Organic Reactions (Russ. Ed.), p. 80. United Scientific and Technical Press (1935).

[8] P.A.Petyunin and N.G.Panferova, J.Gen.Chem. 17, 504 (1947); J.Gen.Chem., 21, 1544 (1951).

[9] A.Abkin and S.Medvedev, J.Gen.Chem. 4, 1411 (1934).

[10] Kauffmann, Ber., 42, 3482 (1909).

[11] Anvers and Meiyer, Lieb. Ann., 309, 327 (1899).

[12] Reissert and More, Ber., 39, 3304 (1906).

Received September 26, 1949.

Laboratory of Organic Chemistry,
Molotov Pharmaceutical Institute

THE SYNTHESIS OF SOME DERIVATIVES OF NICOTINIC ACID

I. B. Simon

The part played by nicotinic acid as an active factor in activity of living organisms, participating in the oxidative-reduction processes of cell tissue, has been the subject of considerable attention in recent years. It acts as a general stimulant of the manufacture of blood. Its detoxifying and antitoxic action in various types of poisoning (by barbiturates, sulfonylamides, lead, and arsenobenzene) has been established [1]. The varied and beneficial action of nicotinic acid upon the organism is reason enough for synthesizing some of its derivatives, which may display physiological activity. Sadykov and Maximov, [2], for example, describe the synthesis of several derivatives of nicotinic acid coupled with sulfonamides.

The present paper describes the synthesis of the following compounds: N-(nicotinyl)-thiourea hydrochloride,* 2-(nicotinylamide)-thiazole, p-carboxyphenylnicotinylamide,** and p-benzenesulfoacetamide-nicotinylamide.

Nicotinic acid is the initial substance for all these syntheses. We prepared it by one of the methods described by us earlier, i.e., by oxidizing anabasine electrochemically [3], or with sulfuric acid [6], or with a chromic acid mixture [7]. The nicotinic acid was processed with an excess of thionyl chloride, the resultant crude acid chloride (a mixture of the nicotinyl chloride and hydrochloride) was condensed with the corresponding amine in an inert solvent (toluene, pyridine, or xylene). We simplified the method for the amines that were freely soluble in pyridine by not isolating the free crude nicotinyl chloride. The pyridine suspension of nicotinic acid was treated with a slight excess of thionyl chloride, and the resultant solution was heated with a pyridine solution of the amine, after which the end product was precipitated with water. A mixture of the substances secured by these two different methods exhibited no depression of the melting point. The yield of the condensation products remained the same as in the first variant. The properties of the compounds synthesized are listed in the table.

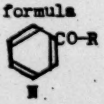
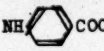
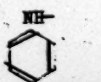
EXPERIMENTAL

N-(Nicotinyl)-thiourea hydrochloride. 10 g of nicotinic acid was placed in a round-bottomed flask fitted with a reflux condenser, a dropping funnel and a stirrer equipped with a mercury seal, and 20 ml of thionyl chloride was added. Then the mixture was heated over a water bath for 1 hour, and the excess thionyl chloride was driven off over a water bath. The crude product consisted of a mixture of the nicotinyl chloride and hydrochloride and was utilizable for further condensations. The yield was 12 g. 5.3 g of the crude nicotinyl chloride was dissolved in 20 ml of toluene and 4.2 g of thiourea was added. The mixture was boiled for 12-14 hours, after which it was cooled, the excess toluene was decanted, and the precipitate was dissolved in 50 ml of alcohol. The solution was filtered and precipitated with twice its volume of ether.

* Douglass [4] mentions nicotinylthiourea very scantily, stating that it may be synthesized by treating an acetone solution of the corresponding mustard oil with ammonia, though the oil is synthesized in such minute quantities that the method is of no more than theoretical interest.

** See following page.

TABLE

No.	Compound	Value of R in the formula 	Melting point: Variant I	Melting point: Variant II	Melting point: Mixture of variants I and II	Overall yield (%)
1	2-(Nicotinylamide)-thiazole		210-211°	210°	210°	60-65
2	p-Carboxyphenyl-nicotinylamide		300-302	300	300	60-62
3	p-Benzenesulfoacetamide-nicotinylamide		248-250	247-248	248	50-55
4	N-(Nicotinyl)-thiourea hydrochloride	$-NHCSNH_2 \cdot HCl$	193-195	-	-	58

The resultant precipitate was filtered out and air-dried. The yield was 7 g, or 58% of the theoretical. The preparation was secured as minute yellowish crystals that were soluble in water and alcohol and insoluble in ether. They decomposed at 193-195°.

4.007 mg substance: 0.68 ml N_2 (22°, 762 mm); 2.986 mg substance: 0.51 ml N_2 (22°, 762 mm); 0.1998 g substance: 0.2072 g $BaSO_4$. 0.2006 g substance: 0.2034 g $BaSO_4$. Found %: N 19.30, 19.42; S 14.58, 14.25. $C_7H_8ON_3SCl$. Computed %: N 19.31; S 14.72.

2-(Nicotinylamide)-thiazole. Variant I. 1.2 g of the nicotinic acid was placed in suspension in 5 ml of anhydrous pyridine, 1 ml of thionyl chloride was added, and the whole was heated over a water bath for 1 hour. Then 1 g of 2-aminothiazole (m.p. 96°), dissolved in 5 ml of anhydrous pyridine, was added, and the mixture was heated for another hour over a water bath. After it had cooled, five times its volume of cold water was added, and it was set aside to stand overnight. The next day the resultant precipitate was filtered out and recrystallized from hot water. The yield was 1.2 g (60%). M.p. 210-211°. The pinkish preparation is soluble in alcohol and hot water, but insoluble in cold water or in ether.

5.399 mg substance: 0.97 ml N_2 (22°, 756 mm); 4.207 mg substance: 0.74 ml N_2 (22°, 756 mm). Found %: N 20.26, 19.94. $C_8H_7ON_3S$. Computed %: N 20.42.

** After the completion of the present research there appeared a paper by Ivanov [5] describing the synthesis of N-nicotinyl-p-aminobenzoic acid by oxidizing p-toluidine with nicotinic acid.

Variant II. 1.4 g of the crude acid chloride of nicotinic acid was dissolved in 5 ml of pyridine, and then 1 g of 2-aminothiazole dissolved in 5 ml of pyridine was added. The mixture was heated over a water bath for 1 hour. When it had cooled, 50 ml of water was added. Upon standing, a red-brown precipitate settled out, which had a m.p. of 210° after recrystallization from hot water. The yield was 1.3 g (65%).

2-Aminothiazole was prepared by condensing monobromoacetal (secured by brominating acetal [8] with thiourea [8]).

p-Carboxyphenylnicotinylamide. Variant I. 1.4 g of nicotinic acid was placed in suspension in 5 ml of anhydrous pyridine, 1.2 ml of thionyl chloride was added, and the mixture was heated over a water bath for 1 hour, after which 1.3 g of p-aminobenzoic acid dissolved in 5 ml of pyridine was added. The subsequent processing was the same as in Variant I for the synthesis of 2-(nicotinylamide)-thiazole. The yield was 1.4 g (60%). The crystals are in soluble in water and slightly soluble in alcohol. M.p. 300-302°.

3.604 mg substance. 0.4 ml N_2 (22°, 756 mm); 4.82 mg substance: 0.545 ml N_2 (22°, 746 mm). Found %: N 12.35, 12.58. $C_{13}H_{10}O_3N_2$. Computed %: N 12.17.

Variant II. This is the same as Variant II for the synthesis of 2-(nicotinylamide)-thiazole. The amount of nicotinyl chloride used was 1.7 g, and that of p-aminobenzoic acid was 1.3 g. The yield was 1.5 g (62%). The crystals had a m.p. of 300°.

p-Benzenesulfoacetamide-nicotinylamide. Variant I. This was the same as the Variant I for the synthesis of 2-(nicotinylamide)-thiazole, using 1.2 g of nicotinic acid, 1.4 ml of thionyl chloride, and 2 g of albucide. The yield was 1.6 g, (50%). M.p. 248-250° after recrystallization from dilute alcohol.

3.806 mg substance: 0.455 ml N_2 (22°, 745 mm); 3.840 mg substance: 0.466 ml N_2 (24°, 747 mm). Found %: N 13.29, 12.96. $C_{14}H_{13}O_4N_3S$. Computed %: N 13.16.

Variant II. This was the same as the Variant II for the synthesis of 2-(nicotinylamide)-thiazole, using 1.7 g of crude nicotinyl chloride and 2 g of albucide. The preparation yield was 1.8 g (56%). The melting point of the preparation was 247-248° after recrystallization from dilute alcohol.

SUMMARY

1. A simple method is described for the synthesis of several derivatives of nicotinic acid by treating it directly with thionyl chloride in pyridine, followed by condensation with the respective amine (without isolating the nicotinyl chloride).

2. Several substituted amides of nicotinic acid have been synthesized, namely: N-(nicotinyl)-thiourea hydrochloride, 2-(nicotinylamide)-thiazole, p-carboxyphenylnicotinylamide, and p-benzenesulfoacetamide-nicotinylamide.

LITERATURE CITED

[1] V.I.Skvortsov. Treatise of Pharmacology, p. 309. Medical Press (1948).

[2] A.S.Sadykov and V.I.Maxim, J.Gen.Chem. 16, 1717 (1946).

[3] I.B.Douglass, L.E.Forman, J.Am.Chem.Soc., 56, 1609 (1934).

[4] Ya.G.Mazover, J.Gen.Chem. 19, 356 (1949).*

* See C.B. Translation, p. 317.

[5] I.B.Simon, Certificate of Authorship No. 70,302 (1947).

[6] I.B.Simon, Certificate of Authorship No. 69,938 (1947).

[7] I.B.Simon, Certificate of Authorship No. 72,668 (1948).

[8] E.Fischer, K. Landsteiner, Ber., 25, 2551 (1892).

[9] I.A.Postovsky, V.I.Khmelevsky, and N.P Bednyagina, J.Appl.Chem. 17, 65 (1944).

Received October 10, 1949.

Ukrainian Institute of Experimental Endocrinology

SYNTHESIS OF AMINOSULFONES

V. Synthesis of Bis-(4-nitrophenylthio)-Alkyl and Aryl Compounds and their Reduction Products

I. Kh. Feldman and T. I. Gurevich

We have secured several compounds of the following type:

$$R_1S-\underset{\displaystyle R}{\underset{|}{C}}H-SR_1 \qquad R_1 = -C_6H_4NO_2;\quad -C_6H_4NH_2;$$

R = aldehyde residue

in order to investigate the chemotherapeutic properties of the aminosulfides and aminosulfones.

Compounds of this type, in which R_1 is an aromatic, aliphatic, or aliphatic-aromatic radical, which did not contain a nitro or amino group were synthesized by Baumann [1] by reacting a mixture of an aldehyde (1 mol.) and a thiol (2 mols) with anhydrous hydrogen chloride. He called the synthesized compounds "mercaptals" Baumann's method was utilized by other authors [2,3,4] to synthesize mercaptals of different structure.

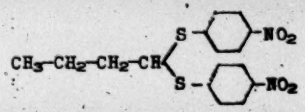
We have condensed aldehydes with p-nitrophenylthiol in a solvent (anhydrous benzene or glacial acetic acid) by passing a current of nahydrous hydrogen chloride through the reaction mixture at 60-80°. We thereby secured the condensation products of p-nitrophenylthiol with n-butyraldehyde, salicylaldehyde, vanillin, and p-dimethylaminobenzaldehyde. All of these products are crystalline substances, more or less deeply yellow in color, insoluble in water and soluble in most organic solvents. They are acid-resistant but are decomposed by alkalies, yielding the respective p-nitrophenylmercaptide. They decompose when an attempt is made to oxidize them to the corresponding β-disulfones, yielding a p-nitrophenylthiol, which is at once oxidized to 4,4'-dinitrodiphenyl disulfide $(p\text{-}NO_2C_6H_4S\text{-})_2$. The synthesized disulfide of the

$$RCH\langle \begin{matrix} SC_6H_4NO_2 \\ SC_6H_4NO_2 \end{matrix}$$

type contains two nitro groups, which are reduced catalytically by hydrogen at room temperature and atmospheric pressure in ethyl alcohol, using Raney's nickel catalyst. The diamino compounds of vanillin and p-dimethylaminobenzaldehyde were secured as chrystalline bases, the diamino compounds of butyraldehyde and salicylaldehyde being secured as dihydrochlorides, however, since their bases proved to be unstable, tarring quickly when exposed to the air.

EXPERIMENTAL

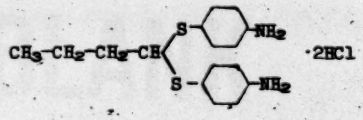
α,α-Bis-(4-nitrophenylthio)-butane



1.8 g (0.025 mol.) of butyraldehyde and 7.75 g (0.05 mol.) of p-nitrophenylthiol were placed in a three-necked flask, with a capacity of about 200 ml, connected to a reflux condenser and a tube for passing gas through the flask. 40 ml of glacial acetic acid was added to the mixture, and anhydrous hydrogen chloride was passed through it at 60-70° (over a water bath) for 2 hours. When the reaction was complete, the current of gas was turned off, the resultant solution solidifying into a yellow crystalline mass when it was stirred with a glass rod after it had cooled to room temperature. The crystals were filtered out in a Buchner funnel, the yield being 5.4 g (60%, based on the ammount of aldehyde employed). Crystallization from acetic acid yielded light yellow needles with a m.p. of 86-87°, freely soluble in hot acetic acid, ethyl acetate, benzene, and chloroform, less so in cold acetic acid, alcohol, and ether, and altogether insoluble in water.

Found %: N 7.47. $C_{16}H_{16}O_4N_2S_2$. Computed %: N 7.69.

α,α-Bis-(4 aminophenylthio)-butane dihydrochloride.

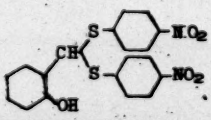


2 g of the α,α-bis-(4-nitrophenylthio)-butane was reduced catalytically with hydrogen in 60 ml of ethyl alcohol containing 4 g of Raney's nickel catalyst at room temperature and atmospheric pressure. 750 ml of hydrogen was absorbed (738 ml being called for theoretically). The catalyst was filtered out, and an alcoholic solution of hydrogen chloride was added to the alcoholic solution of the diamino compound until its reaction was acid, after which most of the alcohol was driven off in vacuum, and the dihydrochloride was recovered with anhydrous ether. This yielded 1.4 g of the amine dihydrochloride (70% yield).

The dihydrochloride was a crystalline yellow precipitate (minute stubby bars under the microscope) with a m.p. of 193-195° (with decomp.). The product is freely soluble in alcohol and in water.

Found %: N 7.32; S 17.02. $C_{16}H_{20}N_2S_2 \cdot 2HCl$. Computed %: N 7.42; S 16.87.

Bis-(4-nitrophenylthio)-2'-hydroxybenzal;

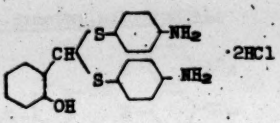


3 g (0.025 mol.) of salicylaldehyde and 7.6 g (0.05 mol.) of p-nitrophenylthiol were reacted with gaseous hydrogen chloride in benzene for 2 hours at 80° in the apparatus described above. When the reaction was over, most of the benzene was driven off in vacuum (until crystallization set in). As the reaction mixture cooled to room temperature crystals settled out, which were filtered out on a Buchner funnel. The yield was 7.9 g (76% of the theoretical, based on the aldehyde used for the reaction). Recrystallization from chloroform

yielded light-yellow lamellae with a m.p. of 144-145°. The product is soluble in benzene, chloroform, alcohol, and acetic acid, but insoluble in water or ether.

Found %: N 6.82; S 15.48. $C_{19}H_{14}O_5N_2S_2$ Computed %: N 6.76; S 15.44.

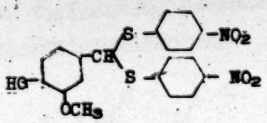
Bis-(4-aminophenylthio)-2'-hydroxybenzal dihydrochloride.



3 g of bis-(4-nitrophenylthio-2'-hydroxybenzal was reduced catalytically with hydrogen in 80 ml of ethyl alcohol containing 6 g of Raney's nickel catalyst at atmospheric pressure and room temperature. 960 ml of hydrogen was absorbed (974 ml being called for theoretically). The catalyst was filtered out, and an alcoholic solution of hydrogen chloride was added to the alcoholic diamine solution until its reaction was acid; then most of the alcohol was driven off in vacuum. As the solution was left to stand, 2 g of yellow crystals (minute needles) with a m.p. of 187-189° (with decomposition) settled out. The melting point was not affected by recrystallization from alcohol. The yield was 67%.

Found %: N 6.57; S 14.34. $C_{19}H_{18}ON_2S_2 \cdot 2HCl$. Computed %: N 6.55; S 14.98.

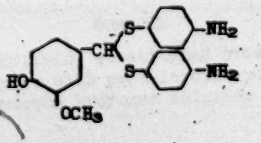
Bis-(4-nitrophenylthio)-3'-methoxy-4'-hydroxybenzal.



3.8 g (0.025 mol) of vanillin and 7.6 g (0.05 mol) of p-nitrophenylthiol were reacted with anhydrous hydrogen chloride in benzene at 80° for 2 hours in the apparatus described previously. When the reaction was over, most of the benzene was driven off in vacuum, causing a yellow crystalline precipitate to settle, totaling 10 g (90% yield, based on the aldehyde used for the reaction). Recrystallization from alcohol yielded light-yellow lamellae with a m.p. of 152-153°, soluble in benzene, acetone, and chloroform, less so in alcohol and glacial acetic acid, and insoluble in water.

Found %: N 6.47; S 14.9. $C_{20}H_{16}O_6N_2S_2$. Computed %: N 6.30; S 14.41.

Bis-(4-aminophenylthio)-3'-methoxy-4'-hydroxybenzal,

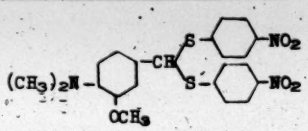


4 g of bis-(4-nitrophenylthio)-3'-methoxy-4'-hydroxybenzal was reduced catalytically at room temperature and atmospheric pressure with hydrogen in 80 ml of ethyl alcohol containing 8 g of Raney's nickel catalyst, 1200 ml of hydrogen being absorbed (1210 ml was called for theoretically). The catalyst was filtered

out, and most of the alcohol was driven off in vacuum; when the residue was allowed to stand, a crystalline precipitate weighing 2.0 g (60% yield) settled out. Recrystallization from alcohol yielded elongated yellow prisms with a m.p. of 151-152°. The diamino compound is freely soluble in alcohol, chloroform, and acetone and sparingly in ether and water.

Found %: N 7.55; S 16.77. $C_{20}H_{20}O_2N_2S_2$. Computed %: N 7.29; S 16.66.

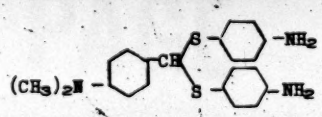
Bis-(4-nitrophenylthio)-4'-dimethylaminobenzal,



3.7 g (0.025 mol.) of paradimethylaminobenzaldehyde and 7.4 g (0.05 mol) of paranitrophenylthiol were reacted with gaseous hydrogen chloride in benzene under the conditions specified above for the preceding experiments. When the reaction was over, the solution was cooled to room temperature, a yellow, noncrystalline, sticky mass that was insoluble in benzene settling to the bottom of the flask. The benzene was decanted, and the remaining mass was treated with hot water, after which it crystallized, the yield being 7.9 g (72%). Recrystallization from chloroform yielded golden quadrangular lamellae with a m.p. of 174-175°. The product is freely soluble in chloroform and acetic acid, less so in alcohol, and insoluble in water, ether, or benzene.

Found %: N 9.61; S 14.76. $C_{21}H_{19}O_4N_3S_2$. Computed %: N 9.52; S 14.51.

Bis-(4-aminophenylthio)-4'-dimethylaminobenzal,



3.5 g of bis-(4-nitrophenylthio)-4'-dimethylaminobenzal was reduced catalytically with hydrogen under the conditions set forth in the preceding experiments, 1080 ml of hydrogen being absorbed (1067 ml called for theoretically). The catalyst was filtered out, and the alcoholic solution was heated to the boiling point; minute, light-yellow needles with a m.p. of 148-147° settled out when it cooled, the melting point remaining unchanged after recrystallization from alcohol. The yield was 2.7 g (90%). The product is freely soluble in chloroform and acetone, less so in alcohol, and insoluble in water or ether.

Found %: N 10.85. $C_{21}H_{23}N_3S_2$. Computed %: N 11.02.

SUMMARY

1. Four bis-(4-nitrophenylthio) substituted products have been synthesized by condensing several aldehydes with paranitrophenylthiol. The condensation was effected by passing anhydrous hydrogen chloride through the reagents in a solvent.

2. Four bis-(4-aminophenylthio) substituted products have been synthesized from the bis-(4-nitrophenylthio) substituted derivatives by reducing them catalytically with hydrogen at room temperature and atmospheric pressure in ethyl alcohol containing Raney's nickel catalyst.

LITERATURE CITED

[1] E.B umann, Ber., 18, 883 (1885).

[2] E.Fromm, Lieb. Ann., 253, 135 (1889).

[3] Th. Posner, Ber., 36,,299 (1903).

[4] R.L.Schreiner, H.S.Struck, W.J.Jorison, J.Am.Soc., 52, 2060 (1930).

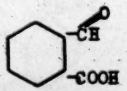
December 14, 1948.

SYNTHESES OF AMINOSULPONES

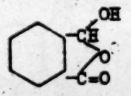
VII. Pseudo Thio Ethers of Orthoaldehydic Acids and Their Derivatives

I. Kh. Feldman and T. I. Gurevich

Pursuing our research [1] on securing β-disulfides by condensing aldehydes with p-nitrophenylthiol, we tested this reaction with phthalaldehydic and opianic acids. We know [2] that o-aldehydic acids sometimes react in their aldehyde form and sometimes in the phthalide form.

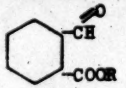


Aldehyde form

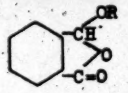


Phthalide form

In the former case we get normal, so-called α-compounds (α-ethers, α-acid halides), while in the second we get pseudo compounds (ψ-ethers, etc.).



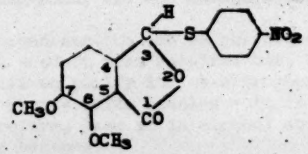
α-ether



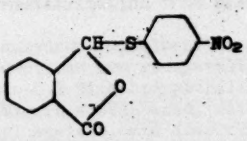
ψ -ether

The latter, that is the ψ-ethers, are formed when alcohols are reacted directly with o-aldehydic acids.

In our work with paranitrophenylthiol, we have found that it reacts with o-aldehydic acids like an alcohol, yielding the respective ψ-thio ethers of these acids. Paranitrophenylthiol was condensed with the o-aldehydic acids in anhydrous dichloroethane or glacial acetic acid, a current of anhydrous hydrogen chloride being passed through the reaction mixture at 60-80°. No matter whether one or two moles of the thiol were used per mole of the o-aldehydic acid, we always secured products, which proved upon analysis to contain one thiol group, i.e., ortho aldehydic acids react with paranitrophenylthiol to form ψ-thio ethers (I and II):

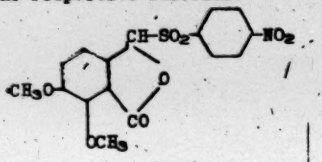


(I)

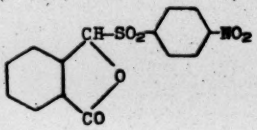


(II)

The thio ethers were oxidized with perhydrol in a mixture of glacial acetic acid and acetic anhydride. Bis-(4-nitrophenylthio)-alkyl or aryl substituted derivatives were not oxidized to sulfones [1], whereas 4-nitrophenylthio-6,7-dimethoxyphthalide and 4-nitrophenylthiophthalide were smoothly oxidized, yielding the respective sulfones:

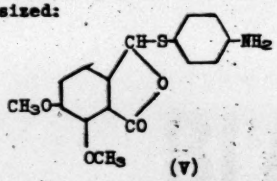


(III)

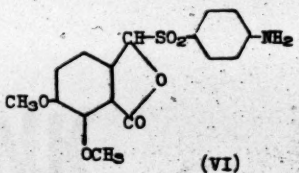


(IV)

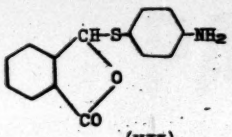
The nitro compounds of the thio ethers and sulfones were catalytically reduced with hydrogen at room temperature and atmospheric pressure in ethyl alcohol containing Raney's nickel catalyst, the following amino compounds being synthesized:



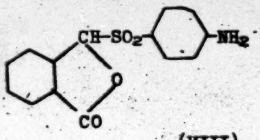
(V)



(VI)



(VII)



(VIII)

EXPERIMENTAL

4-Nitrophenylthio-6,7-dimethoxyphthalide (I). 4.2 g of opianic acid (0.02 mol), 3.1 g of 4-nitrophenylthiol, and 30 ml of glacial acetic acid were placed in a three-necked flask, fitted with a reflux condenser, a thermometer, and an inlet tube for gas. When the temperature of the mixture, heated over a water bath, had reached 80°, a current of hydrogen chloride was passed through it. The deposit gradually dissolved. Toward the close of the reaction, which lasted about 2 hours, an abundant white precipitate was thrown down. It was filtered out on a Buchner funnel, yielding 4.5 g of 4-nitrophenylthio-6,7-dimethoxyphthalide (70% yield, based on the opianic acid used. M.p. 173-174°. The melting point did not change after recrystallization from acetic acid.

The same condensation can be performed in anhydrous dichloroethane, but the resultant product then requires one, and sometimes two recrystallizations from acetic acid to purify it. 4-Nitrophenylthio-6,7-dimethoxyphthalide crystallizes as minute white needles – it is soluble in acetic acid, dichloroethane, and chloroform, less so in alcohol and ethyl acetate, and insoluble in water, ether, or benzene.

Found %: C 55.44; H 4.20; N 4.16; S 9.36. $C_{16}H_{13}O_6NS$. Computed %: C 55.33; H 3.75; N 4.04; S 9.22.

4-Nitrophenylsulfone-6,7-dimethoxyphthalide (III). 3.5 g (0.01 mol) of 4-nitrophenylthio-6,7-dimethoxyphthalide, 20 ml of glacial acetic acid, and 10 ml of acetic anhydride were placed in a flask fitted with a stirrer and a thermometer, which was chilled externally with ice and stirred while 7 ml of 30% perhydrol was added a drop at a time. The temperature of the reaction mixture was kept at about 5°. After addition was complete, the reaction mass was stirred for an hour at the same temperature, and then the temperature was gradually raised to 55-60° by heating the flask over a water bath, the reaction continuing at the latter temperature for another 3 hours. Not all the precipitate dissolved, though its appearance changed. When the reaction was over, the solution was poured into an equal volume of water, the resulting precipitate being filtered out. This yielded 2.1 g from the reaction mixture and 0.35 g from the mother liquor after it had been evaporated in vacuum, i.e., a total of 2.45 g (65% yield). Crystallization from glacial acetic acid yielded rhombic lamellae with a m.p. of 171-172°. The product is soluble in acetic acid, chloroform, and ethyl acetate, sparingly soluble in alcohol, and insoluble in water or ether.

Found %: N 3.74; S 8.51. $C_{16}H_{13}O_8NS$. Computed %: N 3.69; S 8.44.

4-Aminophenylthio-6,7-dimethoxyphthalide (V). 3 g of 4-nitrophenylthio-6,7-dimethoxyphthalide was reduced catalytically with hydrogen at room temperature and atmospheric pressure in ethyl alcohol containing 6 g of Raney's nickel catalyst. 630 ml of hydrogen was absorbed (600 ml being called for theoretically). This yielded 1.8 g (67%) of a white crystalline substance as elongated tetrahedral prisms, with a m.p. of 162-163° after recrystallization from alcohol. The amine is soluble in alcohol and acetone, and insoluble in water.

Found %: C 60.61; H 4.82; N 4.41; S 9.96. $C_{16}H_{15}O_4NS$.
Computed %: C 60.56; H 4.73; N 4.40; S 10.08.

4-Aminophenylthio-6,7-dimethoxyphthalide hydrochloride consisted of minute white crystals with a m.p. of 182-183° (with decomposition) that are insoluble in water or alcohol.

Found %: HCl 11.01 (potentiometric titration).
$C_{16}H_{15}O_4NS \cdot HCl$. Computed %: HCl 10.32.

4-Aminophenylsulfone-6,7-dimethoxyphthalide (VI). 3 g of 4-nitrophenylsulfone-6,7-dimethoxyphthalide was reduced catalytically with hydrogen under the conditions specified above, using 6 g of the Raney catalyst. 600 ml of hydrogen was absorbed, as against the 535 ml called for theoretically. The catalyst was filtered out of the hot solution, and a white crystalline precipitate settled out in the form of elongated needles with a m.p. of 211-212°. The yield was 2 g (72%). The melting point was not changed by recrystallization from alcohol. The amine is soluble in alcohol, chloroform, and ethyl acetate, and insoluble in ether or water.

Found %: N 4.07; S 8.79. $C_{16}H_{15}O_6NS$. Computed %: N 4.01; S 9.17.

4-Aminophenylsulfone-6,7-dimethoxyphthalide hydrochloride consisted of white crystals with a m.p. of 198-199° (with decomposition), insoluble in alalcohol or water.

Found %: N 3.43; $C_{16}H_{15}O_6NS \cdot HCl$. Computed %: N 3.63.

4-Nitrophenylthiophthalide (II). 1.5 g of phthalaldehydic acid (0.01 mol), 1.6 g of 4-nitrophenylthiol (0.01 mol), and 20 ml of glacial acetic acid were

placed in a three-necked flask, fitted with a reflux condenser, a thermometer, and an inlet tube for gas. The mixture was heated over a water bath to 80°, and anhydrous hydrogen chloride was passed through it for 2 hours. Heating dissolved the deposit in the flask, a light-yellow precipitate being thrown down again toward the end of the reaction. Upon cooling, the precipitate was filtered out, yielding 2 g (77%) of light yellow pyramidal crystals with a m.p. of 173-174°, the m.p. rising to 177-178° after recrystallization from ethyl acetate. The product is soluble in acetic acid, ethyl acetate, and chloroform, sparingly soluble in alcohol, and insoluble in water.

Found %: N 4.90; S 11.49. $C_{14}H_9O_4NS$. Computed %: N 4.91; S 11.15.

4-Nitrophenylsulfonephthalide (IV). 2.9 g of 4-nitrophenylthiophthalide (0.01 mol), 20 ml of glacial acetic acid, and 10 ml of acetic anhydride were placed in a flask fitted with a stirrer and a thermometer and oxidized with perhydrol under the conditions set forth for the oxidation of 4-nitrophenylthio-6,7-dimethoxyphthalide. The reaction mass dissolved when heated, a precipitate gradually settling out toward the end of the reaction, which was then filtered out, yielding 2.5 g of a white crystalline product with a m.p. of 186-187° (87% yield). The melting point did not change after recrystallization from acetic acid. The product is soluble in acetone, chloroform, alcohol, and acetic acid, less so in ether and ethyl acetate, and insoluble in water.

Found %: N 4.32; S 10.30. $C_{14}H_9O_6NS$. Computed %: N 4.39; S 10.00.

4-Aminophenylthiophthalide (VII). 2 g of 4-nitrophenylthiophthalide was reduced catalytically with hydrogen under the conditions specified above, 4 g of the Raney catalyst being used and 490 ml of hydrogen being absorbed as against the 470 ml called for theoretically. When reduction was complete, the catalyst was filtered out of the hot solution, which was allowed to cool. As it cooled, white lamellar crystals with a m.p. of 160-161° settled out, the yield being 1.6 g (90%). The melting point was not affected by recrystallization from alcohol. The amine is soluble in alcohol and acetone and insoluble in water.

Found %: N 5.26; S 12.30. $C_{14}H_{11}O_2NS$. Computed %: N 5.44; S 12.45.

4-Aminophenylsulfonephthalide (VIII). 2 g of 4-nitrophenylsulfonephthalide was reduced catalytically with hydrogen under the conditions specified above, using 4 g of the Raney catalyst and absorbing 450 ml of hydrogen as against the 420 ml called for theoretically. Filtering out the catalyst and driving off part of the alcohol in vacuum yielded 1.6 g of the amino compound with a m.p. of 221-222° (90% yield). Recrystallization from alcohol did not affect the melting point of the product. The amine is soluble in alcohol and acetone and insoluble in water.

Found %: N 4.79; S 11.08. $C_{14}H_{11}O_4NS$. Computed %: N 4.84; S 11.07.

SUMMARY

1. Condensation of phthalaldehydic and opianic acids with p-nitrophenylthiol has yielded the respective ψ-thio ethers, which were converted into sulfones by oxidation.

2. The corresponding amino compounds were secured by reducing the thio ethers and sulfones.

LITERATURE CITED

[1] I. Kh. Feldman and T.I.Gurevich, J.Gen.Chem. 21, 1371 (1951).

[2] H.Meyer, Ber., 22, 76 (1901); V.M.Rodionov and A.M.Fedorova, Ber., 59, 2949 (1926); A.Kipral, Ber., 60, 382 (1927); V.M.Rodionov and S.I.Kanevskaya, Bull. Soc. Chim. France (5), 1, 653 (1936).

Received December 14, 1948.

All-Union Research Institute of Pharmaceutical Chemistry.

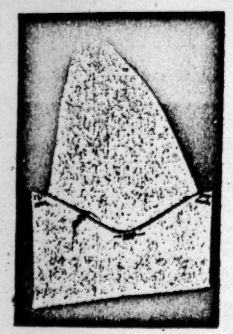


Fig. 6.

4. X-Ray photo of the second solid solution sample, reduced at 500°.

5 X-Ray photo of the second solid solution sample, reduced at 600°.

6. X-Ray photo of the second solid solution sample, reduced at 700°.

1. X-Ray photo of solid solution sample I, reduced at 500°.

2. X-Ray photo of solid solution sample II, reduced at 600°.

3. X-Ray photo of solid solution sample III, reduced at 700°

7 X/Ray photo of the third solid solution sample, reduced at 500°.

8. X-Ray photo of the third solid solution sample, reduced at 600°.

9. X-Ray photo of the third solid solution sample, reduced at 700°.